A TEXT BOOK OF
Analytical Chemistry

DEGREE COURSE

Prof. S. P. BANERJEE

THE NEW BOOK STALL
CALCUTTA 700 009

TABLE OF

	Oxide or Hydroxide	Carbonate	Sulphide	Fluoride	Chloride
Silver	d.n.	d.n.	d.n.	w.	i
Mercurous	d.n.	d.n.	—	d.n.	c.n.
Lead	d.n.	d.n.	d.n.	d.n.	w.
Mercuric	d.h.	d.h.	a.r.	d.n.	w.
Bismuth	c.h.	d.h.	d.n.	d.h.	d.h.
Cuprous	c.h.	—	c.n.	c.h.	c.h.
Cupric	d.h.	d.h.	d.n.	d.h.	w.
Cadmium	d.h.	d.h.	d.h.	w.	w.
Stannous	d.h.	—	c.h.	w.	w.
Stannic	i.	—	c.h.	w.	w.
Arsenious	d.h.	—	c.n.	—	w.
Antimonious	d.h.	—	c.h.	w.	d.h.
Antimonic	c.h.	—	c.h.	w.	w.
Aluminium	d.h.	—	—	w.	w.
Chromic	d.h.	—	—	d.h.	w.
Ferrous	d.h.	d.h.	d.h.	w.	w.
Ferric	d.h.	—	—	w.	w.
Zinc	d.h.	d.h.	d.h.	w.	w.
Manganese	c.h.	d.h.	d.h.	d.h.	w.
Cobalt	c.h.	d.h.	c.n.	w.	w.
Nickel	d.h.	d.h.	c.n.	d.h.	w.
Calcium	w. : d.h.	d.h.	d.h.	i.	w.
Strontium	w. : d.h.	d.h.	d.h.	d.h.	w.
Barium	w.	d.h.	d.h.	d.h.	w.
Magnesium	d.h.	d.h.	d.h.	d.h.	w.

N.B.
1. All sodium, potassium and ammon
2. All nitrates and nitrites except basi
3. Natural silicates are generally insol silicates, which have not been ignit
4. Below is given the meaning of the

w.—water.
d.h.—dilute hydrochloric acid.
c.h.—concentrated hydrochloric
d.n.—dilute nitric acid.

SOLUBILITIES

Bromide	Iodide	Borate	Phosphate	Arsenite	Arsenate	Chromate	Sulphate
i	i	d.n.	d.n.	d.n.	d.n.	d.n.	w.
c.n.	c.n.	d.n.	d.n.	d.n.	d.n.	d.n.	d.n.
w.	w.	d.n.	d.n.	d.n.	d.n.	d.n.	i.
w.	c.n.	d.h.	d.h.	d.h.	d.h.	d.h.	d.h.
d.h.	d.h.	d.h.	d.h.	—	d.h.	d.h.	w.
c.h.	c.h.	—	—	—	—	—	—
w.	—	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w.	w.	d.h.	d.h.	—	d.h.	d.h.	w.
w.	w.	d.h.	d.h.	d.h.	d.h.	—	w.
w.	d.h.	—	c.h.	—	c.h.	—	—
—	—	—	—	—	—	—	—
d.h.	d.h.	—	—	—	—	—	—
—	—	—	—	—	—	—	—
w.	w.	d.h.	d.h.	—	d.h.	d.h.	w.
w.	—	d.h.	d.h.	w.	d.h.	—	w.
w.	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w.	—	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w.	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w.	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w.	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w.	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w.	w.	d.h.	d.h.	d.h.	d.h.	w.	w. : c.h.
w.	w.	d.h.	d.h.	d.h.	d.h.	w.	i.
w.	w.	d.h.	d.h.	d.h.	d.h.	d.h.	i.
w.	w.	d.h.	d.h.	d.h.	d.h.	w.	w.

ium salts are soluble in water.
c nitrates and silver nitrite are soluble in water.
uble; some, which are hydrated are decomposed by conc. HCl. But artificial
ed undergo decomposition on treatment with dil. HCl.
abbreviations used in the above table:

c.n.—concentrated nitric acid
a.r.—aqua regia.
acid.
i.—insoluble.

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ANALYTICAL CHEMISTRY

for

Degree Course

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Dedicated
to the
memory
of my
beloved
Mother

PREFACE

The present book aims to meet the needs of Degree Course students, who enter college with a smattering of knowledge in the rudiments of science, and as such, feel unequal to the task of coping with the fairly advanced syllabus of collegiate studies. Analytical Chemistry, in particular, is a stiff hurdle and many a beginner comes to grief in their efforts to negotiate this hurdle. Much careful planning has, therefore, gone into the making of this book so as to obviate the difficulties of beginners and render the operations and principles of analytical chemistry as simple and intelligible as possible. The author has every hope that the book will help the students to a living interest in and a good grasp of the subject.

In writing this book the author has had unstinted help and encouragement from many educationists and friends to all of whom he acknowledges his indebtedness. Special thanks are due to the publishers, Sri Mohendranath Paul for the eager interest he has taken in the publication.

Criticisms of whatever shortcomings the book may have are cordially invited from learned colleagues and it is hoped that the next edition of the book will be immensely benefited by their kind and wise suggestions.

City College,
Chemical Laboratory,
January, 1988.

AUTHOR

CONTENTS

PART I INORGANIC QUALITATIVE ANALYSIS

CHAPTER PAGE

I. A systematic scheme for qualitative analysis 1
II. Preliminary tests for basic radicals 3
III. Preliminary tests for acidic radicals 23
IV. Examination of cations in solution 34
V. Examination of anions in solution 76
VI. Treatment of insoluble residue (or sample) 87
Specimen records of analytical results 97

PART II ORGANIC QUALITATIVE ANALYSIS

Class determination:

I. Scheme 111
II. Detection of elements 112
III. Detection of functional groups 117
Specimen records of analytical results 130

Reactions and tests of some common organic compounds :

I. Reactions and tests 136
II. Identification, General 169
Specimen records of analytical results 190
III. Identification, when given pure 195

PART III QUANTITATIVE INORGANIC ANALYSIS

I. General considerations 207
II. *Volumetric (Titrimetric) analysis* : 211
Principle: general instructions: standard solutions
III. Acidimetry and alkalimetry 217
IV. Oxidimetry and reductimetry: 227
(α) Oxidation with $KMnO_4$, (β) Oxidation with $K_2Cr_2O_7$, (γ) Iodometry
V. Titrimetric analysis of some special samples 247
VI. *Gravimetric estimation*: 250
Iron, Silver and Sulphate

PART IV QUANTITATIVE ORGANIC ANALYSIS

Formalin, Aniline, Glucose 259

PART V PREPARATION OF ORGANIC COMPOUNDS

1. Iodoform. 2. Sulphanilic acid. 3. Acetanilide
4. *p*-bromoacetanilide. 5. Tribromophenol. 6. *p*-nitracetanilide.
7. *p*-nitraniline. 8. Acetylsalicylic acid. 9. Phthalimide.
10. Naphthol orange. 11. Nitrobenzene. 12. *m*-dinitrobenzene.
13. Anisole. 271

Sample Questions for Viva voce 280

APPENDIX

1. Table of Atomic Weights 330
2. Reagents 330-335
Logarithms

CHAPTER I

A SYSTEMATIC SCHEME FOR QUALITATIVE ANALYSIS

A systematic process of qualitative analysis of every inorganic substance comprises :

1. Preliminary examination for basic radicals;
2. Preliminary examination for acidic radicals;
3. Special tests for interfering acids;
4. Preparation of solution for examination of basic radicals (or cations);
5. Examination of solution for basic radicals;
6. Preparation of solution for examination of acid radicals (or anions);
7. Examination of solution for acid radicals;
8. Determination of probable composition.

Examination of the substance should be carried out in the above order and after the completion of the analysis a probable composition of the sample is to be suggested.

It should be noted here that some prefer a modification* of the above scheme of analysis. But in this treatise, however, we will confine ourselves to the discussion of operation in the order stated above.

Whatever be the order, unless otherwise stated, don't feel tempted at any stage of your operations to be side-tracked into carrying out one or the other confirmatory reactions leaving aside your systematic work.

Before proceeding with the systematic analysis, the physical characteristics of the substance supplied should be carefully noted. Observe, if possible, whether the substance is crystalline or amorphous. Note that a substance cannot be said to be amorphous or crystalline unless it is thoroughly examined, *e.g.*, by microscope, X-ray analysis, etc. Note also whether it has any characteristic colour or odour and whether it is comparatively light or heavy. [Compounds of mercury and lead are heavy and those of magnesium and aluminium are usually light.]

**Modified scheme*: Before proceeding with the examination of cations in solution, the examination of anions in solution is carried out.

Colours of commonly known Inorganic substances are listed below:

Red:	HgO, HgI_2, HgS, As_2S_2, Sb_2S_3, Pb_3O_4, Cu_2O, CrO_3, Ag_2CrO_4.
Pink:	Hydrated salts of cobalt and of manganese with few exceptions.
Brown:	Chromates of iron and copper, Fe_2O_3, Fe_3O_4, $Fe(OH)_3$, PbO_2 (may appear black also), CdO, Ag_3AsO_4, SnS, Mn_2O_3, Mn_3O_4 .
Yellow:	Chromates, ferric chloride, CdS (may appear orange-red also), As_2S_3,SnS_2, AgI, PbI_2, Hg_2I_2, PbO, Bi_2O_3, HgO, $FePO_4$ (very light yellow).
Black:	Ag_2S, PbS, CuS, HgS, Bi_2S_3, FeS, CoS, NiS, CuO, FeO, Fe_3O_4, CoO (olive green, may appear black), Co_3O_4, NiO, Ni_2O_3. MnO_2. There is one variety of Sb_2S_3 which is black.
Blue:	Hydrated cupric salts; anhydrous cobalt salts.
Green:	Cupric copper in some salts (rest are blue), some salts of ferrous iron, chromium and of nickel; Cr_2O_3, $Cr(OH)_3$ and Hg_2I_2.
Orange Red:	Dichromates, Sb_2S_3.

Besides, the colour of the solution obtained on dissolving the substance in a particular solvent for analysis (and any change of colour on dilution) should be noted, as it may often give useful indication.

Colours of the solution : Coloured ions are best seen in dilute solution. The following colours are exhibited by the ions present in the dilute solution :

Yellow:	Ferric iron, chromates, ferrocyanides [note that the yellow colour is often observed in conc. HCl and *aqua regia* solutions, which may not contain above ions].
Blue:	Cupric copper.
Orange Red:	Dichromates [colour of the solution vary from yellow to orange-red depending on concentration and *pH*].
Pink:	Cobalt, manganese.
Green:	Ferrous iron, trivalent chromium, nickel, manganates.

It should be remembered that in the case of a mixture of substances having different colours the above colour chart may not be of any help and may even be misleading. But, when the presence of all the acidic and basic radicals in a sample is known [*i.e.*, after the completion of the analysis], a student knowing the solubility of different constituents of the mixture in different solvents [solubility chart] will find the colour chart very helpful in suggesting a probable composition of the sample supplied.

CHAPTER II

PRELIMINARY TESTS FOR BASIC RADICALS

If the substance supplied be not in a state of fine division, it should be reduced to fine powder in a mortar before proceeding with the following tests. The following tests should be carried out quickly, more or less in the order given below and should never be omitted as it often gives us an idea of the nature of the sample to be analysed and the method to be adopted for its subsequent examination:

1. Closed tube test, *i.e.*, heating in a dry test tube;
1.(*a*) & (*b*) Special closed tube tests;
2. Heating in oxidising flame on charcoal block;
2.(*a*) Cobalt nitrate test;
2.(*b*) Borax bead test;
3. Heating in reducing flame on charcoal block;
4. Flame test;
5. Microcosmic bead test ;
6. Some special tests.

1. Heating in a test tube

Take a little quantity of the dry powdered sample in a clean and dry test tube in such a way that not a speck of it adheres to the sides of the test tube. Now heat the tube cautiously; at first gently, and then strongly in the non-luminous Bunsen flame, holding the tube in an almost horizontal position; note carefully any change that takes place.

Observations	Inferences
A. The substance changes colour:	
(*i*) Blackening	Salts of Cu Ni,Mn, Co and, Fe.
(*ii*) Yellow when hot, white when cold	ZnO and many Zn compounds.
(*iii*) Yellowish-brown when hot, white or light yellow when cold, but without fusion on strong heating.	SnO_2

Observations	Inferences
(*iv*) Orange-yellow or reddish-brown when hot, dull yellow when cold (the substance being fusible at red heat).	Bi_2O_3
(*v*) Yellow when hot, yellow when cold. The substance fuses at red heat.	PbO and some Pb compounds.
(*vi*) Dark brown but infusible when hot, dark brown when cold.	CdO and many Cd compounds.
(*vii*) Dark red or nearly black when hot, reddish-brown when cold.	Fe_2O_3
(*viii*) Red when cold, turns black on slight heating. But when heated strongly:	Pb_3O_4 HgO
(*a*) Forms shining mirror on cooler parts of the test tube.	HgO
(*b*) Turns reddish-brown.	Pb_3O_4
(*ix*) Green when both hot and cold.	Cr_2O_3 and some chromium compounds.
B. The substance does not change colour:	
(*i*) The substance is white and shows no change at all.	Al, Ba, Ca, Sr, Mg.
(*ii*) The substance fuses and undergoes solidification on cooling.	Many compounds of alkalis and alkaline earth metals.
(*iii*) The substance first swells, then melts and finally solidifies.	Borax, alums, etc.

N.B. The changes of colour are sometimes due to simple physical change (*e.g.*, Fe_2O_3), sometimes due to loss of water of crystallisation (*e.g.*, blue copper sulphate becoming white) followed or accompanied by decomposition of the substance by heat, sometimes to mere decomposition of the substance into metal (*e.g.*, change of red HgO into shining mirror of Hg), sometimes due to conversion of the substance into oxides of metal [*e.g.*, colourless $Pb(NO_3)_2$ changing to yellow PbO] and sometimes due to oxidation, *e.g.*, red Cu_2O changes to black CuO by heating.

Observations	Inferences
C. Elimination of water takes place:	
The substance gives off water, which condenses in drops on the cooler upper portion of the test tube.	
(*i*) Condensed water is acid to litmus.	Free volatile acids, acid salts and anhydrides and also the readily decomposable salts of strong acids.
(*ii*) Condensed water is alkaline to litmus.	Ammonium compounds.
(*iii*) Condensed water is neutral to litmus.	Water of crystallisation, water of hydration, etc.
D. Gas or vapours given off:	
(*i*) Reddish-brown gas, which does not turn CS_2 layer brown.	NO_2 from nitrates or nitrites of heavy metals.
(*ii*) Reddish-brown gas—turns CS_2 brown and starch-KI paper blue.	Bromine from bromides of heavy metals and mixture of bromides and oxidising agents.
(*iii*) Yellowish-green gas having the smell of bleaching powder—turns starch-KI paper blue and bleaches moist litmus paper.	Chlorine is evolved from chlorides in presence of oxidising agents, unstable chlorides, *e.g.*, of copper.
(*iv*) Violet vapours of iodine is evolved (condensing to black crystals The vapour turns starch paper blue.	Free iodine and certain iodides.

Observations	Inferences
(*v*) Colourless, odourless gas is evolved. It turns lime water milky.	Carbon dioxide from carbonates, bicarbonates.
(*vi*) Colourless, odourless gas rekindles a glowing splint.	Oxygen from chlorates, bromates, iodates, nitrates, peroxides, perchlorates and permanganates.
(*vii*) Colourless gas having the smell of rotten eggs, turning lead acetate paper black.	H_2S from hydrated sulphides, acid sulphides.
(*viii*) Colourless gas having the odour of burning sulphur, turning dichromate paper green.	SO_2 from sulphites, thiosulphates and certain sulphates.
(*ix*) Colourless gas having pungent odour of ammonia, turning mercurous nitrate paper black. The gas also blues red litmus paper.	Ammonia from ammonium salts.
E. A sublimate is formed:	Volatile compounds, *e.g.*, several compounds of Hg, As, Sb, NH_4^+, etc.
(a) The substance melts and yields a white sublimate.	$HgCl_2$, $HgBr_2$, $PbCl_2$, Sb_2O_3 $SnCl_2$.

Observations	Inferences
(b) *A white sublimate, the substance does not melt before volatilisation.*	Hg_2Cl_2, Hg_2Br_2, Free boric acid, Ammonium compounds with volatile acids, arsenites, As_2O_3.
(c) *The substance gives a coloured sublimate.*	
(i) Original colour of the substance is *red* or *black*; Sublimate—*black*, turns *red* on prolonged trituration.	HgS
(ii) Original substances is *red*, sublimate *yellow*, turns *red* when rubbed with a glass rod.	HgI_2
(iii) Original substance is *yellow*; sublimate *dark reddish-brown* when hot, red to *reddish-yellow* when cold.	As_2S_3.
(iv) Original substance is *golden yellow* in colour, *yellow sublimate* is formed.	SnS_2
(v) Original substance is *red* or *black* or *snuff coloured*, sublimate is almost *black* when hot, *orange* when cold.	Sb_2S_3, Sb_2S_5
(vi) Original substance is *bluish-black crystals*, evolution of *violet* vapours; *blue-black* sublimate.	Iodine
(vii) *Grey* sublimate or a metallic shining *mirror*, which coalesces into globules of mercury on rubbing with a glass rod.	Mercury oxide, some compounds of mercury that are transformed into oxides easily.

N.B. The observations (D) recorded in pages 5-6 help to suggest the acidic radicals and hence should be considered along with preliminary examination for the acidic part of the substance described later on.

1. (a) Special closed tube test :

If a white sublimate is formed in experiment 1, *i.e.*, closed tube test, mix a portion of the original substance on a piece of paper, with four times its volume of anhydrous Na_2CO_3. Take a portion of this mixture in a clean and dry test tube in such a way that not a speck of the substance adheres to the sides of the tube and heat it strongly.

Observations	Inferences
(*i*) Characteristic smell of ammonia; the gas turns mercurous nitrate paper black and red litmus paper blue.	Ammonium compounds.
(*ii*) A grey mirror coalesces into globules of Hg on being rubbed with a glass rod.	Hg compounds
(*iii*) Garlic odour; shining black mirror, which does not give globules on rubbing with a glass rod.	Compounds of arsenic [exception —As_2S_2, As_2S_3 and arsenates.]

1. (b) *If no satisfactory result is obtained in experiment* 1. (*a*), heat the substance with a mixture of Na_2CO_3 and KCN (or charcoal powder). Take a mixture of one part of the dry substance with 4 times its volume of anhydrous Na_2CO_3 and KCN in a clean and dry test tube and finally heat.

Observations	Inferences
A. A mirror is formed:	
(*i*) Shining mirror, which coalesces into globules of mercury on being rubbed with a glass rod.	Hg compounds
(*ii*) Black mirror, no globules on rubbing with a glass rod.	As compounds
(*ii*) Shining metallic mirror.	Cd compounds

Observations	Inferences
B. A bead is formed:	
(*i*) Metallic bead marks paper	Pb compounds
(*ii*) Bead does not mark paper	Compounds of Ag[*], Sb[†], Sn, Bi.

N.B. *Caution*: Don't inhale on any account the fumes that may be evolved in the experiment. Discard the test tube.

In case a bead is formed recover the bead by breaking the test tube and making it free from KCN after thoroughly washing the bead with water.

Some reactions in the special closed tube test:

Mercury compounds:

(*a*)

$$HgCl_2+Na_2CO_3 = HgCO_3+2NaCl$$

$$HgCO_3 = \underset{\text{(red)}}{HgO}+CO_2$$

$$2HgO = 2Hg+O_2$$

(*b*)

$$Hg_2Cl_2+Na_2CO_3 = Hg_2CO_3+2NaCl$$

$$Hg_2CO_3 = Hg_2O+CO_2$$

$$2Hg_2O = 4Hg+O_2.$$

Ammonium Compounds:

$$2NH_4Cl+Na_2CO_3 = (NH_4)_2CO_3+2NaCl$$

$$(NH_4)_2CO_3 = 2NH_3+CO_2+H_2O.$$

Heating the substance with Na_2CO_3 and charcoal (or KCN) facilitates the conversion of the compound into the corresponding metal, *e.g.*,

$$SnO_2+2KCN = Sn+2KCNO$$

$$2As_2O_5+10KCN = As_4+10KCNO.$$

---

[*] In case of Ag, the bead will have a white shining appearance.

[†] In this test a black mirror may sometimes be obtained with Sb-compounds. The mirror is insoluble in NaOCl but that obtained from As-compounds is soluble in NaOCl.

2. Heating in oxidising flame on charcoal block

Heat a little of the substance in a small cavity scooped at one end of a charcoal block in the oxidising flame* with a mouth blow-pipe.

Observations	Inferences
(*a*) *Deflagration takes place*	Nitrates, Nitrites, chlorates, iodates, permanganates, i.e., substances rich in oxygen.
(*b*) *The substance decrepitates*	Bromides, iodides, chlorides of alkalis, crystalline salts, *e.g.*, KCl, NaCl, etc.
(*c*) *The substance fuses readily*	
(*i*) and sinks into the charcoal.	Salts of alkalis and some salts of alkaline earths.
(*ii*) and a bead is obtained which does not sink into the charcoal.	Borates, phosphates, silicates.

**R.F.* and *O.F.*: Reduce the size of the flame to about two inches long by regulating the supply of gas. Close the air hole of the burner and see that the flame is luminous. Hold the nozzle of the mouth blow-pipe just *outside* the flame and after the cheeks have blown out to their fullest extent blow gently and steadily from cheeks so as to project the inner bluish cone on to the substance taken in the charcoal groove. This is heating by a reducing flame (R.F.). Don't blow vigorously as the flame will then become oxidising.

To get an oxidising flame (O.F.) keep the air hole open. Hold the nozzle of the mouth blow-pipe in the *centre* of the flame and blow gently but somewhat more vigorously than before. Allow the extreme tip (which is almost invisible) of the flame to fall upon the substance taken in the charcoal groove.

Observations	Inferences
(d) *An incrustation is formed surrounding the groove on charcoal block.*	
(*i*) White incrustation (dense white fumes also evolve).	NH_4^+, Hg and As compounds.
(*ii*) White incrustation with a blue edge.	Sb compounds
(*iii*) Incrustation—yellow when hot, white when cold.	Compounds of Zn, Sn.
(*iv*) Incrustation deep yellow when hot, sulphur yellow when cold.	Pb compounds
(*v*) Reddish-brown incrustation at a distance away from the hot area.	Cd compounds
N.B. Ash of charcoal block may be mistaken for incrustation.	
(e) *A bead is formed*	Compounds of Ag, Pb, Bi, Sb etc.
(*i*) White malleable bead which marks paper.	Pb compounds
(*ii*) Bead does not mark paper.	Compounds of Ag, Bi, Sb.
(f) *Residue left on charcoal is coloured*	
(*i*) Residue—Black and infusible.	Compounds of Cu, Fe, Mn, Co, Ni.
(*ii*) Residue—Brown and infusible.	Fe, Mn compounds.
(*iii*) Residue—Green and infusible.	Cr compounds
(*iv*) Residue—Red (or yellow) and fusible.	Compounds of Pb, Bi, CrO_4''.
N.B. Coloured residues are often obtained from coloured salts.	
(g) *White infusible residue, incandescent when hot* is left on charcoal	CaO, SrO, BaO, MgO, SnO_2, ZnO, Al_2O_3 and SiO_2.

N.B. When a white (white, light yellow or grey) residue is left on charcoal, perform cobalt nitrate test [expt. 2. (*a*)]. When the substance supplied is coloured and/or whenever a coloured residue is left on charcoal in the above test, try borax bead test [expt. 2. (*b*)]. But if the substance shows tendency of reduction, *e.g.*, in the case of Pb, Ag, etc. perform charcoal reduction test (expt. 3).

2. (a) Cobalt nitrate test

Moisten the white residue left on charcoal with a drop or two of dilute solution of cobalt nitrate and heat again in the oxidising flame by means of a mouth blow-pipe.

Observe the colour of the residue.

Observations	Inferences
(*i*) Blue or violet residue	Al compounds, phosphates, borates, arsenates and silicates
(*ii*) Green residue.	Zn compounds
(*iii*) Bluish-green residue	Sn compounds
(*iv*) Grey residue.	Compounds of Ca, Sr and Ba.
(*vi*) Pink residue.	Mg compounds

N.B. Don't add *excess* of cobalt nitrate $Co(NO_3)_2$ for carrying out the experiment, because CoO is formed by decomposition of $Co(NO_3)_2$ on heating. If this oxide be formed in excess, the excess of it will be converted under experimental condition into cobaltic oxide Co_3O_4, which is black in colour. This will mask the distinctive colours produced by combination of CoO with the oxide (residue) by its own black colour.

Reactions in cobalt nitrate test

Certain oxides—the white residual mass formed from compounds under examination—on combination with cobalt oxide derived from cobalt nitrate develop remarkable, characteristic colour.

$$2Co(NO_3)_2 \rightarrow 2CoO + 2N_2O_4 + O_2$$

$$CoO + Al_2O_3 \rightarrow \underset{\text{Thenard's blue}}{CoAl_2O_4\text{(blue)}}$$

$$CoO + ZnO \rightarrow \underset{\text{Rinmann's green}}{CoZnO_2\text{ (green)}}$$

With MgO a compound possibly having similar composition (MgO, CoO) is formed.

2. (b) Borax bead test

Clean up a platinum wire first by heating it in the non-luminous Bunsen flame and dipping it repeatedly into borax. Heat the wire again until the borax swells up and forms a clean transparent glassy bead. Hold the wire in the flame in such a manner that the bead moves from end to end. Finally, jerk the bead off the wire while hot. Make a loop at the end of of a platinum wire thus cleansed by winding it at the tip of a blow-pipe. Heat the loop in the non-luminous Bunsen flame and dip it in fresh borax, which adheres to it. Heat the loop again until a bead is formed as before. Touch the substance with the hot bead so that *only a little* of the substance adheres to the bead. Heat the bead again first (*a*) in the *oxidising* flame, then (*b*) in the *reducing* flame. Note the colour of the bead in each case.

Observations		Inferences
Colour of the bead		
Oxidising flame	Readucing flame	
(*i*) Green when hot but blue when cold.	Opaque red on cooling (helped by the addition of a drop of $SnCl_2$ to the blue bead obtained in the O.F.).	Cu-compounds

Observations		Inferences
Colour of the bead		
Oxidising flame	Reducing flame	
(*ii*) Sapphire blue when both hot and cold.	Sapphire blue	Co-compounds
(*iii*) Reddish-yellow while hot but becomes yellow on cooling.	Green bead, when hot or cold.	Fe-compounds
(*iv*) Green when both hot and cold.	Green when both hot and cold.	Cr-compounds
(*v*) Amethyst violet.	Colourless	Mn-compounds
(*vi*) Brown when hot, light brown when cold.	Grey or black and opaque after cooling	Ni-compounds

N.B. Carry out the borax bead test with a very small quantity of the substance. But, if the colour is not prominent, take a little more of the substance for this test by touching the substance with the hot bead. Too much of the substance forms saturated bead and the bead may become opaque or so dark coloured that it cannot be detected easily.

Reactions in Borax bead test:

Borax on being heated, swells up, loses its water of crystallisation and finally forms a transparent glass-like bead, which is a mixture of sodium meta-borate and boric anhydride.

$$Na_2B_4O_7,10H_2O = Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3.$$

When the bead is heated with certain metallic salts, the latter loses its water of crystallisation if there be any and is finally converted into oxide, which, on reaction with B_2O_3 and $NaBO_2$, produces meta-borate and ortho-borate. The coloured bead is due to the characteristic colour of the meta-borate. Thus, with copper salt (in the oxidising flame) the following reactions occur:

$$CuSO_4, 5H_2O = CuSO_4 + 5H_2O$$

$$CuSO_4 = CuO + SO_3$$

$$CuO + B_2O_3 = \underset{\text{meta-borate}}{Cu(BO_2)_2}. \qquad CuO + NaBO_2 = \underset{\text{ortho-borate}}{NaCuBO_3}.$$

In the reducing flame, the following reactions occur:

The meta-borate in contact with carbon of the reducing flame undergoes reduction first to colourless cuprous meta-borate and ultimately to metallic copper, which is red in colour.

$$2Cu(BO_2)_2 + C = Cu_2(BO_2)_2 + B_2O_3 + CO$$

$$Cu_2(BO_2)_2 + C = 2Cu + B_2O_3 + CO$$

$$B_2O_3 + 2NaBO_2 = Na_2B_4O_7.$$

Hence in some cases (as in the case of copper) borates corresponding to varying stages of oxidation of the metal are obtained.

The borate corresponding to higher oxide of metal is obtained in the O.F. and the borate corresponding to the lower oxide is obtained in the R.F. Iron gives ferrous and ferric; Mn gives manganous and manganic borates, -ic in the *oxidising* and -ous in the *reducing* flame. Thus the different coloured beads are formed because of the formation of meta-borates (having different colours) corresponding to the varying stages of oxidation. Note that in the case of compounds of nickel, $Ni(BO_2)_2$ corresponding to NiO, the only basic oxide of nickel is formed in the oxidising flame, when the bead turns brown; this borate then undergoes reduction to metallic nickel in the reducing flame and an opaque bead results. Chromium and cobalt yield $Cr(BO_2)_3$ and $Co(BO_2)_2$ respectively in the oxidising flame. $Cr(BO_2)_3$ is not reduced by R.F. and colour of cobaltous compound is blue; hence in the case of Cr-salts one and the some colour is observed both in O.F. and R.F. and a blue coloured bead is obtained in both the flames with cobalt compounds.

3. Heating in reducing flame on charcoal block

Mix a little of the substance with about 3 to 4 parts of anhydrous sodium carbonate on a piece of paper. Take a portion of the mixture in a cavity cut out on a piece of charcoal and heat it in the reducing flame by means of a mouth blow-pipe.

Observations	Inferences
A. An incrustation without metallic bead	
(*i*) Brown incrustation.	Cd
(*ii*) White incrustation and fumes having garlic smell.	As
(*iii*) White incrustation, which becomes yellow while hot. Again turns white on cooling.	Zn
B. A metallic bead with incrustation	
(*i*) Yellow incrustation; bead malleable and marks paper	Pb
(*ii*) Yellow incrustation; bead pinkish, white and brittle.	Bi
(*iii*) White incrustation; bead—white and brittle.	Sb
C. A metallic bead without incrustation	
(*i*) Scattered bead; white and malleable	Sn
(*ii*) Grey magnetic mass.	Fe, Ni, Co
(*iii*) White malleable bead.	Ag
(*iv*) Red flakes and spongy mass	Cu
D. White infusible residue, but becomes incandescent on heating	Ba, Sr, Ca, Mg, Al, Si,
E. Green residue left on charcoal	Cr

N.B. 1. Salts of all sulphur acids are reduced to sulphides by this treatment. Hence to detect sulphur acids:

(*i*) Extract the residue with a little water and filter. Add a few drops of the filtrate to a freshly-prepared sodium nitroprusside solution. An unstable violet coloration indicates the presence of *sulphur compounds.*

(*ii*) Treat the fused mass (residue) with dilute HCl; smell of rotten eggs indicates the presence of *sulphur compounds.*

2. If the presence of Sn and Sb compounds be suspected, heat in the reducing flame a little of the substance on charcoal with Na_2CO_3 and KCN instead of Na_2CO_3 alone, since beads of Sn and Sb are not formed easily.

3. Make separate cavity for separate substance.

Reactions in Charcoal reduction test:

On reaction with Na_2CO_3 the substances are converted into carbonates and these are, for the most part, decomposed into oxides and carbon dioxide. The oxides of the metals may remain unchanged or may undergo further decomposition or reduction. Thus with silver sulphate

$$[Ag_2SO_4+Na_2CO_3 = Ag_2O+CO_2+Na_2SO_4$$
$$2Ag_2O+C = 4Ag+CO_2]$$

a white metallic bead is obtained. Note that the decomposition of Ag_2O into metallic silver occurs even in absence of charcoal. Oxides of lead, copper, etc. are reduced to metallic condition by charcoal but oxides of Ca, Sr, Ba and Al are not reduced.

$$CuSO_4+Na_2CO_3 = CuCO_3+Na_2SO_4$$
$$CuCO_3 = CuO+CO_2$$
$$2CuO+C = 2Cu+CO_2$$

In the case of chromium salts, non-reducible Cr_2O_3 is formed.

$$Cr_2(SO_4)_3+3Na_2CO_3 = Cr_2O_3+3CO_2+3Na_2SO_4$$

(Green coloured)

KCN helps the reduction of SnO_2, which is otherwise difficultly reduced.

$$SnO_2+2KCN=Sn+2KCNO.$$

Oxides of arsenic, cadmium and zinc are easily reduced to respective metals, which being volatile come in contact with the oxidising zone of the flame whereby they are oxidised to difficultly volatile oxides. The oxides are then deposited as incrustation surrounding the charcoal cavity. Thus with Cd-salts

$$CdSO_4+Na_2CO_3=CdCO_3+Na_2SO_4, \quad CdCO_3=CdO+CO_2$$
$$2CdO+C=2Cd+CO_2. \quad 2Cd+O_2=2CdO.$$

4. Flame test

Moisten a clean* platinum wire with pure and concentrated

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*Cleanse the platinum wire first by heating with borax (*see* borax bead test), if necessary (*i.e.*, to remove the persistent colours) then by heating with concentrated HCl. [Dipping of the pt.-wire in conc. HCl and heating should be done alternately till it fails to impart any colour to the non-luminous flame.]

HCl and then dip the tip of the wire into a portion of the substance taken out on a watch glass or a piece of paper when some particles adhere to the wire. [Do not dip the wire directly into the original sample, which in that case will be contaminated with HCl.] Now hold the tip of the platinum wire at the base of the non-luminous flame and gradually raise the wire. Continue alternate moistening with concentrated HCl and heating for a few minutes*; note the colour imparted to the flame.

Observations	Inferences
(*i*) Golden yellow but invisible through blue glass.	Na
(*ii*) Light violet but intense violet red (or, crimson) through blue glass.	K
(*iii*) Brick red (or dull red) and transient; but light green when seen through blue glass	Ca
(*iv*) Persistent apple green, but bluish-green through blue glass.	Ba
(*v*) Persistent crimson, but purple through blue glass.	Sr
(*vi*) Bluish-green.	Cu, PO_4'''
(*vii*) Bluish-white flashes.	Bi, Pb
(*viii*) Green.	Boric acid
(*ix*) Green flashes.	As, Sb, Zn

N.B. 1. Observe the flame coloration first with the naked eye and then through the thickness of two cobalt blue glasses. Because in the case of some mixtures, the different constituent may give different flame colorations and one-colour may mask

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*In some cases, *e.g.*, $CaSO_4$, $SrSO_4$, $BaSO_4$ the flame coloration is obtained with difficulty. It is best on such occasion to heat a little of the compound on a platinum wire in the upper reducing flame and then moistening it with concentrated HCl and heating again in the non-luminous flame. The desired result is often obtained after continuing the experiment for a few minutes. But phosphates of alkaline earths very rarely impart any colour to the flame.

that owing to another, *e.g.*, sodium obscures the flame coloration of potassium.

A vastly improved method for observing the potassium flame is to view it through a cubic glass vessel containing a strong solution of chrome alum. Complete disappearance of sodium flame occurs but the flame due to potassium becomes prominent.

2. Use is made only of the tip of the pt.-wire as compounds of Pb, Bi, As, Sb, etc., if heated on platinum wire may be converted into respective metals, which, if formed, make the pt.-wire brittle by forming alloys with it. Hence, if the above-mentioned compounds be suspected by earlier expt. (*cf.* charcoal reduction test), carry out the flame test on asbestos thread.

3. Chloride of metals being more volatile than other compounds impart characteristic colours to flame more readily and that is why HCl is used in flame test.

5. Microcosmic bead test

Make a bead on the loop of a cleansed platinum wire by heating microcosmic salt [sodium ammonium phosphate $Na(NH_4)HPO_4,4H_2O$]. Carry out the experiment exactly as in the borax bead test, and note the changes that may occur.

Observations		Inferences
Oxidising flame	Reducing flame	
(*i*) Blue when both hot and cold.	Blue when both hot and cold.	Co
(*ii*) Green while hot, blue on cooling.	Reddish-brown and opaque.	Cu
(*iii*) Green when both hot and cold.	Green when both hot and cold.	Cr
(*iv*) Amethyst violet.	Colourless	Mn
(*v*) Solid particles are found swimming about in the bead while hot, but a cob-web-like structure on cooling.		Silica, silicates. SnO_2.

N.B. The absence of 'swimming about' of solid particles or 'cob-web-like' structure in the bead is no definite indication of the absence of a silicate, since some silicates dissolve completely in the bead and consequently no 'swimming about' of solid particles is observed.

Reactions in microcosmic bead test:

The microcosmic salt $Na(NH_4)HPO_4, 4H_2O$ on being heated is ultimately converted into sodium meta-phosphate $NaPO_3$.

$$Na(NH_4)HPO_4{,}4H_2O = Na(NH_4)HPO_4 + 4H_2O;$$
$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O.$$

Sodium meta-phosphate dissolves many metallic oxides yielding ortho-phosphate, which have often characteristic colours. Thus the salts of manganese and cobalt yield a violet and blue bead respectively.

$$CoO + NaPO_3 = NaCoPO_4 \text{ (blue colour).}$$

Like borax bead test this test is performed in both the flames (O.F. and R.F.). Some ortho-phosphates remain unaffected and some undergo reduction. Thus with copper compounds the ortho-phosphate formed in O.F. is reduced to metallic copper in R.F.

$$CuNaPO_4 + C = Cu \text{ (red colour)} + NaPO_3 + CO.$$

Sodium meta-phosphate exhibits practically no tendency to react with acidic oxide particularly silica. Some silicates, if heated on microcosmic bead—SiO_2 is liberated. SiO_2 being insoluble in the phosphate bead swims about in the molten bead.

$$CaSiO_3 + NaPO_3 = NaCaPO_4 + SiO_2.$$

And there are many silicates, as has already been said, that dissolve completely in the bead.

6. Some Special Tests

(i) Fusion test for Mn and Cr :

Experiment:

Take a little solid caustic soda on a mica foil or broken porcelain and heat to melt it. Now sprinkle a little of the substance under investigation (suspected to contain Mn and/or Cr) and a little KNO_3 or $KClO_3$ on molten NaOH. Continue heating till the mass fuses completely. Cool and observe the colour of the residue.

Observations	Inferences
(*a*) Green mass	Mn-compounds
(*b*) Yellow mass	Cr-compounds

(*a*) Dissolve the green mass in water and filter. Acidify the filtrate with dil. HNO_3. Development of pink colour shows the presence of **Mn.**

(*b*) Dissolve the yellow mass in water and filter. Acidify the filtrate with dil. acetic acid; boil off CO_2 if any, and add lead acetate soln. A yellow ppt. shows the presence of **Cr.**

(ii) Test for Ammonia:

Experiment.

Take a little of the sample and sodalime on a piece of paper; press it in-between folds of paper and rub. Open the paper and take the smell.

Observation	Inference
Smell of ammonia	Ammonium compounds

N.B. 1. If Mn- and Cr- compounds occur together, the emerald-green colour observed in the borax bead test indicates the presence of chromium; but may mask the amethyst violet colour due to Mn. In the fusion test the reverse is true; the green mass of manganate indicates the presence of Mn, but may mask the yellow colour of chromate.

On such occasion to detect chromium, dissolve the residue (from fusion test) in water, add a few drops of alcohol, warm and filter. Acidify the filtrate with acetic acid. Boil off any carbon dioxide and add silver nitrate. A red precipitate or a red coloration indicates the presence of chromium.

2. Ammonia may also be detected by heating the substance under investigation with caustic soda and holding over it a glass rod moistened with HCl, when a *dense white fume* of NH_4Cl results. But heating with caustic soda, results in rapid evolution of ammonia which may escape unnoticed, specially when ammonium compound is present in small quantity. Hence. to detect NH_4^+ radical it is better to perform the test in

Acc. no. - 15484

the manner stated in Expt. 6 (*ii*) and testing the gas evolved not only by smell alone but also with mercurous nitrate paper, which turns *black* or with a glass rod moistened with HCl as stated above.

Reactions in special tests:

(*i*) Chromium and manganese compounds on reaction with alkali carbonate and oxygen (or, NaOH+oxygen) of which the latter is derived from KNO_3 (or $KClO_3$) are ultimately converted into sodium chromate (yellow in colour) and sodium manganate (green in colour) respectively.

$$2Cr_2O_3+4Na_2CO_3+3O_2=4Na_2CrO_4+4CO_2$$

$$MnO+Na_2CO_3+O_2=Na_2MnO_4+CO_2$$

$$2Cr_2O_3+8NaOH+3O_2=4Na_2CrO_4+4H_2O$$

$$2MnO_2+4NaOH+O_2=2Na_2MnO_4+2H_2O.$$

(*ii*) Sodalime is obtained by slaking quicklime with caustic soda solutions. When ammonium salt is heated with sodalime the following reaction occurs :

$$(NH_4)_2SO_4+2NaOH=Na_2SO_4+2NH_3+2H_2O.$$

For special test of tin dioxide, students are to consult the treatment of insoluble substances, given later.

CHAPTER III

PRELIMINARY TESTS FOR ACIDIC RADICALS

The following tests together with some special tests should be carried out at this stage in the order given below so as to get an idea regarding the nature of the sample to be analysed. This will help a student to devise a procedure to be followed for the wet analysis of the substance.

1. Treatment of the substance with dil. H_2SO_4 or dil. HCl.
2. Treatment of the substance with conc. HCl.
3. Treatment of the substance with conc. H_2SO_4.
4. Treatment of the substance with conc. H_2SO_4 and MnO_2.
5. Treatment of the substance with conc. H_2SO_4 and Cu-turnings
6. Some special tests.

Preliminary tests for acidic radicals

Experiment 1:

Take a little of the substance in a test tube. Add dil. H_2SO_4 (or dil. HCl) to it. Observe the effect, first when cold and then on warming.

Observations	Inferences
(*i*) *Evolution of colourless and odourless gas takes place—*	
Effervescence in the cold. The evolved gas turns lime water milky.	Carbonate. Bicarbonate.
(*ii*) *Evolution of colourless gas with distinct odour—*	
(*a*) Evolution of colourless gas having the smell of burning sulphur; turns filter paper moistened with acidified potassium dichromate green or blue-green.	Sulphite
(*b*) Evolution of colourless gas, smell of rotten eggs; blackens a strip of filter paper moistened with lead acetate solution.	Sulphide
(*c*) Same as in (*a*) together with the deposition of white or light yellow sulphur, which makes the solution turbid.	Thiosulphate

Observations	Inferences
(*iii*) *Evolution of coloured gas with characteristic odour—*	
(*a*) Evolution of reddish-brown fumes; slight irritating smell, turns starch-potassium iodide paper bluish-black.	Nitrite
(*b*) Evolution of yellowish-green gas; smell of bleaching powder, bleaches litmus paper and blues starch-potassium iodide paper.	Hypo-chlorite

N.B. 1. With carbonates of Pb and alkaline earth metals better results are obtained, if dil. H_2SO_4 be substituted by dil. HCl.

2. Sulphur dioxide also produces turbidity, when passed through lime water. Hence mere production of turbidity is no definite proof of the presence of carbonate, which should be reported only if sulphite and thiosulphate are found absent.

3. All sulphides are not decomposed by dil. acid.

4. Evolution of brown fumes of nitrogen dioxide results on the addition of acid even in the *cold* (i.e., without warming) to a solid nitrite.

Experiment 2:

Take a little of the substance in a test tube and warm it with conc. HCl.

Observations	Inferences
All the anions discussed above yield much the same results as with dil. HCl (*cf.* Expt. 1), in addition to which the following may be observed.	
(*i*) Evolution of greenish-yellow gas; irritating smell; blues starch-potassium iodide paper.	Presence of oxidising agents.
(*ii*) Evolution of violet vapours.	Iodide in presence of oxidising agent.
(*iii*) Evolution of brown vapours.	Bromide in presence of oxidising agent.

Experiment 3:

Take a little of the substance in a dry test tube and warm it with conc. H_2SO_4.

Observations	Inferences
In addition to observations made under Expt. 1 the following changes may be observed:	
(*i*) Evolution of colourless gas, corrodes glass; a drop of water on a glass rod when held in the fumes becomes turbid due to deposition of silicic acid; the mixture in the tube has an oily appearance.	(HF from) Fluoride
(*ii*) Evolution of colourless gas; pungent smell; dense white fumes of NH_4Cl produced, when a glass rod moistened with NH_4OH solution is held at the mouth of the test tube.	(HCl from) Chloride
(*iii*) Evolution of reddish-brown gas, condensing to red drops on cooler parts of the test tube; turns CS_2 brown and moist starch paper orange-red.	(HBr & Br_2 from) Bromide
(*iv*) Evolution of violet vapours, condensing to black solid; turns CS_2 violet and blues starch paper.	(HI and I_2 from) Iodide
(*v*) Evolution of reddish-brown fumes, condenses to brown drops of liquid. On passing into NaOH solution, a yellow solution is obtained, which, after acidification with acetic acid, gives a yellow precipitate with lead acetate solution.	(CrO_2Cl_2 from) a mixture of Chloride and Chromate
(*vi*) Evolution of brown vapours not condensing to liquid; colour deepens on addition of copper turnings.	(NO_2 from) Nitrate, Nitrite
(*vii*) Evolution of yellowish-green gas, irritating smell; blues starch-iodide paper and bleaches litmus paper	(Chlorine from) a mixture of chloride and oxidising agent.

N.B. 1. Observation (*ii*), i.e. *dense white fumes with* NH_4OH described above under Expt. 3 is not specific for HCl, it is also a test for HNO_3.

2. There are some carbonates which are decomposed by dil. H_2SO_4; some may require conc. H_2SO_4 and some may require heat to boiling even with conc. H_2SO_4. Better results are ensured by constant stirring of the mass while warming it with acid. But if heated strongly, conc. H_2SO_4 decomposes evolving SO_2 and SO_3. In such a case mere turning of baryta water milky should not be regarded as a confirmatory test for carbonate.

3. The presence of reducing agent may lead to the evolution of SO_2 gas, when H_2SO_4 is used. [This SO_2 is formed by the reduction of H_2SO_4 by reducing agent like $SnCl_2$, Hg_2Cl_2., etc.].

4. There are some sulphides, *e.g.*, sulphide of Hg, As, etc. which are not decomposed by acids. Hence, some special tests should be carried out for them.

5. In carrying out the test for fluoride the test tube should be scrupulously dry.

Experiment 4:

Warm in a test tube a little of the substance with conc. H_2SO_4 and MnO_2.

Observations	Inferences
(*i*) Evolution of greenish-yellow gas, pungent and irritating smell of chlorine.	Chlorine from Chlorides.
(*ii*) Evolution of reddish-brown gas having very irritating smell; condenses to red drops at the upper cooler parts of the test tube.	Bromine from Bromides.
(*iii*) Evolution of violet vapours with characteristic pungent and irritating smell, condenses to black crystals up the test tube.	Iodine from Iodides.

Experiment 5:

Warm in a test tube a little of the substance with conc. H_2SO_4 and copper turnings.

Observations	Inferences
Evolution of brown fumes	Nitrate, Nitrite, Bromide.

Some special test for detection of acid radicals

Some special tests should be carried out at this stage, since the experiments described so far for the detection of acid radicals fail to give any clue as to the presence of some acid radicals.

Experiment I. (*i*):

Heat gently in a test tube a little of the substance with 1 : 1 HCl and a few granules of zinc*; hold a moist lead acetate paper at the mouth of the test tube.

Observation	Inference
Lead acetate paper turns black.	Sulphide+

N.B. Since chromate, nitrite, etc. destroy the evolved H_2S, the above test of sulphide fails in the presence of these acid radicals. In such a case, it is advisable to boil the substance with Na_2CO_3 solution and test for H_2S by treating the residue with zinc and hydrochloric acid.

Experiment I. (*ii*):

Fuse a little solid NaOH on a mica foil or in a broken porcelain crucible. Sprinkle a little of the substance on the molten mass and heat‡ again, cool, extract with water. cool. filter and divide the filtrate into two parts:

(*a*) To one part of the filtrate add a few drops of a dilute solution of freshly prepared sodium nitroprusside.

(*b*) Acidify the other part with dil. HNO_3; boil off CO_2, add $AgNO_3$ solution.

Observations	Inferences
(*a*) A deep violet or pink colour appears.	Sulphide
(*b*) A white or yellow precipitate insoluble in HNO_3.	Halide

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*If As or Sb be suspected it is better to perform the experiment in fume cupboard; as highly poisonous arsine or stibine may be formed in this reaction. Moreover, blank expt. should always be performed with this zinc, as commercial zinc is sometimes found to be contaminated with sulphide.

+Some sulphides are not decomposed by diluted and even by the conc. acids (HCl or H_2SO_4). Hence the necessity of performing this test for sulphides. Note again that besides S'', other sulphur containing substances, such as SO_3'', S_2O_3'', etc. also liberate H_2S under this condition. Hence in their (SO_3'', S_2O_3'' etc.) presence this test cannot be a confirmatory one for sulphides.

‡If As or Ag be suspected heat gently for a short time.

Experiment II. (a) :

Extract a little of the substance with dil. HNO_3 and filter. Add a few drops of the solution thus prepared to an excess of ammonium molybdate solution taken in a test tube and then add 2-3 c.c. of conc. HNO_3. Let it stand, warm and finally heat, if necessary.

Observation	Inference
A canary yellow precipitate.	Phosphate, and arsenate.

N.B. (*i*) The formula $(NH_4)_3[PMo_{12}O_{40}]$ is assigned to yellow crystalline precipitate of ammonium phosphomolybdate.

$$Na_2HPO_4+12(NH_4)_2MoO_4+23HNO_3$$
$$=(NH_4)_3[PMo_{12}O_{40}]+21NH_4NO_3+2NaNO_3+12H_2O.$$

Similar reaction is given by arsenates on boiling. Note that if the extraction be done with conc. HNO_3, arsenite also will respond to this test. Silicates give only a yellow solution on boiling. Besides, white molybdic acid may separate out on boiling. Hence while testing for phosphate the solution should not be heated to a temperature exceeding 40°C.

(ii) In absence of HNO_3 ammonium molybdate is reduced to blue or violet compound by reducing agents.

(iii) The yellow precipitate is soluble in alkalis, ammonia, alkali phosphates and excess of phosphoric acid. Hence excess of reagents, *i.e.*, ammonium molybdate and conc. HNO_3 are to be used.

Experiment II (b) :

Add to the 1 c.c. of dil. nitric acid extract of the sample taken in a test tube 2 c.c. of 15-20% tartaric acid solution followed by 2 c.c. of ammonium molybdate solution. Warm gently and allow to stand for a few minutes.

Observation	Inference
Formation of a yellow precipitate	Phosphate

N.B. AsO_4^{3-} and SiO_3^{2-} do no interfere in this test.

Experiment III. (a) :

Take a little of the substance in a test tube and add about 1 c.c. methyl alcohol. Gently heat the test tube and ignite the issuing gas.

Observation	Inference
The gas burns with a green-edged flame.	Free boric acid

Experiment III. (b):

If no green-edged flame is observed in Expt. III. (a) take a little of the substance in a test tube and make a paste of it with conc. H_2SO_4. Add about 1 c.c. methyl alcohol. Gently heat the test tube and ignite the issuing gas.

Observation	Inference
The gas burns with a green-edged flame.	Borate

N.B. The above test for borate is known as 'alcohol flame test' and since in this experiment free boric acid, if present, also produces the same green-edged flame, the mere production of green-edged flame here is no proof of the presence of borate, which, however, should only be reported if free boric acid is found absent by earlier experiment, *i.e.*, Expt. III (*a*). Copper and barium salts however do not interfere with this test under the *experimental condition*, as they are converted into non-volatile sulphates.

Boric acid reacts with methyl alcohol giving methyl borate, which burns with a green-edged flame.

$$H_3BO_3+3CH_3OH=B(OCH_3)_3+3H_2O$$

Ethyl alcohol can also be used instead of methyl alcohol. But the ethyl borate that is formed in the reaction being less volatile than methyl borate, the use of methyl alcohol is always preferred.

Borates, which are insoluble in water, can, however, be detected even in presence of free boric acid in the following way:

Boil a little of the substance with water and filter. Repeat this process with the residue (if necessary), till it is free from free-boric acid [made known by performing the Expt. III. (*a*)] and then carry out the Expt. III. (*b*) with this residue, when *a green-edged flame* indicates the presence of borate. [*See also* the separation of acid mixture given later.]

Experiment IV:

Warm in a clean and perfectly dry test tube a mixture of the substance with a little silica and conc. H_2SO_4 over a small flame. Hold a glass rod containing a drop of water at its tip at the mouth of the test tube.

Observation	Inference
The drop of water turns turbid. Moreover, oily drops are seen on the walls inside the test tube.	Fluoride

N.B. The turbidity of water drop is due to the deposition of silicic acid, which is formed by hydrolytic decomposition of silicon-tetra-fluoride. The reaction can be illustrated with calcium fluoride. Thus,

$$CaF_2+H_2SO_4 = CaSO_4+2HF$$

$$SiO_2 \text{ (Silica)}+4HF = SiF_4+2H_2O$$

$$3SiF_4+4H_2O = H_4SiO_4+2H_2SiF_6.$$

Note that this expt. may be carried out without addition of SiO_2, since the necessary SiO_2 comes from glass of the test tube.

Experiment V.

Take in a lead basin (crucible) a mixture of the substance and calcium fluoride (in the ratio of 2 : 1 by weight). Add conc. H_2SO_4 to the mixture to make a thin paste. Cover the crucible with a lid having a small opening. Hold a drop of water on a platinum loop over the opening in the lid and subsequently heat the crucible on an asbestos board over a small flame.

Observation	Inference
A wax-like deposit turns the drop of water turbid.	Silicate or silica

N.B. Immediately after the addition of H_2SO_4 to the mixture, the platinum loop carrying the water drop should be held over the opening in the lid of the crucible; because, the mere addition of H_2SO_4 may sometime cause the evolution of volatile SiF_4. Hence in such cases the water drop may not turn turbid if it is held over the opening after heating the mixture.

Experiment VI. (*a*):

Take a little of the solution,* add dil. H_2SO_4 till acid; cool it under a tap; add a little ether (about 0·5 c.c.) and a drop of 3% hydrogen peroxide and shake.

Observation	Inference
The etherial solution is coloured blue, which gradually turns green.	Chromate

N.B. The blue colour is due to the formation of perchromic acid. The blue solution is very unstable and decomposes yielding oxygen and a green solution of a chromic salt. The reaction can be stated in the following way (suppose Na_2CrO_4 has been given):

$$\begin{aligned}
2Na_2CrO_4 &+ H_2SO_4 &&= Na_2Cr_2O_7 &&+ Na_2SO_4 + H_2O\\
Na_2Cr_2O_7 &+ H_2SO_4 &&= H_2Cr_2O_7 &&+ Na_2SO_4\\
H_2Cr_2O_7 &+ 7H_2O_2 &&= 2H_3CrO_8 &&+ 5H_2O\\
2H_3CrO_8 &+ 3H_2SO_4 &&= Cr_2(SO_4)_3 &&+ 5O_2 + 6H_2O.
\end{aligned}$$

Experiment VI. (*b*):

Acidify a portion of the solution* with dil. acetic acid and add lead acetate solution.

Observation	Inference
A yellow precipitate, soluble in dil. HNO_3 and also in caustic soda solution; acetic acid reprecipitates the chromate from the latter solution.	Chromate

---

*Mix a portion of the substance with about 4 parts of Na_2CO_3 and a little water in a beaker; boil for 15 minutes and filter. Take a little of the fitrate and perform the tests for chromate. Reserve the bulk of the filtrate for wet analysis described later on. It should be noted that chromates are usually yellow-coloured substances, yielding yellow-coloured solutions when soluble in water. In presence dil. mineral acids, chromates change into dichromates, which give orange-red solution. [If the substances be soluble in water and free from heavy metals, perform the test with aqueous solution.]

Experiment VII

Mix a little of the substance with about 3 to 4 parts of anhydrous Na_2CO_3. Take a portion of this mixture in a cavity cut on a piece of charcoal and heat it in the reducing flame by means of a mouth blow pipe.

(*a*) Treat a portion of the fused mass (residue) with dil. HCl.

(*b*) Extract another part of the residue with water; filter and add a few drops of the filtrate to a freshly-prepared sodium nitroprusside solution.

Observations	Inferences
(*a*) Evolution of H_2S gas, characterised by rotten egg's smell and blackening of lead acetate paper.	Sulphur acids
(*b*) An unstable violet colouration.	Sulphur acids

N.B. Salts of all sulphur acids, *i.e.*, sulphide, sulphite, thiosulphate and sulphate respond to this test. Salts of these sulphur acids on reaction with sodium carbonate and charcoal in the reducing flame are first converted into sodium sulphide, which (*i*) when reacts with hydrochloric acid gives hydrogen sulphide recognised by its characteristic rotten egg odour and by some such other property as stated already in observations under Expt. VII above, but (*ii*) when reacts with sodium nitroprusside solution an unstable violet coloration due to formation of $Na_4[Fe(CN)_5NOS]$ is developed. Suppose the sample is $BaSO_4$, the reactions that occur are as follows:

$$BaSO_4 + Na_2CO_3 + 2C \text{ (from charcoal)} = BaCO_3 + Na_2S + 2CO_2$$

$$Na_2S + 2HCl = 2NaCl + H_2S$$

$$Na_2S + Na_2[Fe(CN)_5NO] = Na_4[Fe(CN)_5NOS]$$

Note that the latter reaction occurs in presence of alkali solution and neither the hydrogen sulphide solution nor the free gas will give this reaction.

Moreover, the reagent, *i.e.*, sodium nitroprusside solution must be freshly prepared by dissolving the solid of about the size of a mustard seed in little distilled water.

CHAPTER IV

EXAMINATION OF CATIONS IN SOLUTION

Preparation of Solution of the Substance

The next step in the qualitative analysis of an inorganic substance is to prepare a solution of the substance in a suitable solvent (or solvents) for the detection of the basic radical (or radicals) in the wet way. Examine the solubility of the substance in the following solvents in the order given below.

(*i*) Water—cold and boiling; (*ii*) dil HCl—cold and hot; (*iii*) conc. HCl—cold and hot; (*iv*) *Aqua regia* (prepared by mixing one volume of conc. HNO_3 with three volumes of conc. HCl) or conc. HCl and a few particles of $KClO_3$. The procedure for getting the substance in solution is tabulated below.

TABLE 1

Take 0·5—1 gm. of the powdered substance in a beaker; add 50 c.c. of distilled water and boil for a few minutes. Filter hot, if any solid remains undissolved.

Filtrate[1] : Evaporate in a test tube (preferably on a watch glass or in a small basin) a few drops of the filtrate.	**Residue:** Boil the residue with 10 c.c. dil. HCl[2] for a few minutes. If any solid remains add about 5 c.c. conc. HCl and boil[3] again. Filter hot, if there is any residue.

<table>
<tr>
<td rowspan="2">If no residue, reject the filtrate.</td>
<td colspan="2">If any residue, take about 3 c.c. of the solution in a test tube. Add to it a little NH_4Cl and 1 c.c. of conc. solution of sodium phosphate. Make just ammoniacal by adding NH_4OH and heat.</td>
<td colspan="2">Filtrate: If any precipitate[4] comes down on cooling, filter.</td>
<td colspan="2">Residue: Boil the residue with <i>aqua regia</i>[5] (or conc. HCl and $KClO_3$). If there is any residue, filter.</td>
</tr>
<tr>
<td>Precipitation occurs. Examine the solution from group I of General Group separation table.
But before proceeding with the group separation, test the original solution (<i>i.e.</i>, filtrate[1]) with litmus paper, acidic reaction indicates the presence of weakly basic salts like $SnCl_2$ etc.</td>
<td>No precipitation. Group separation in unnecessary. Test the original solution, <i>i.e.</i>, filtrate[1] with litmus paper. If it reacts acidic, H_3BO_3, As_2O_3 may be present. If not acidic Na, K, NH_4^+ present.
If, however, As^{+3} is suspected, it must be looked for and confirmed by usual analysis.</td>
<td>Filtrate: Evaporate* in a test tube a few drops of the filtrate.
(A) If any residue, examine this from Group II of the general group separation table.
(B). If no residue, reject the filtrate.</td>
<td>Residue: Examine the residue according to the table of Group I.</td>
<td>Filtrate: Evaporate* in a test tube a few drops of the filtrate.
(A) if no residue reject the filtrate.
(B) If there is any residue take the filtrate in a basin and evaporate nearly to dryness. Add a little concentrated hydrochloric acid to it and again evaporate to dryness.
Dissove the residue in dilute hydrochloric acid and examine the solution from Group II of the general group) separation table</td>
<td>Residue[6]: Wash the residue well with hot water and examine by the general or special methods as given later, under the heading 'Treatment of insoluble substances'.</td>
</tr>
</table>

*The evaporation should preferably be carried out on a watch glass or in a small basin.

Notes on Table 1

1. Sometimes the filtrate turns turbid on cooling, which does not settle in a short time, but dissolves on addition of a little HCl. This turbidity is due to the formation of oxy-salts of Sn, Sb and Bi. These oxy-salts are formed by hydrolysis of the compounds of these metals. Sometimes white needle-shaped or golden spangles or both may appear in the filtrate when cooled. This indicates the presence of $PbCl_2$ (white needle shape) or $PbBr_2$ (golden spangles) or PbI_2 (golden spangles) or a mixture of these compounds in the original substance.

2. Colloidal sulphur may separate out here on treatment with HCl. This may be due to: (*i*) presence of thiosulphate, (*ii*) presence of sulphide along with sulphite, or, (*iii*) a sulphide together with an oxidising agent. Besides, due to reaction between acid soluble sulphide and a compound of Gr. II metal (if present together) a coloured ppt. may come down here.

3. Sometimes prolonged boiling and subsequent dilution with water followed by boiling again of the dilute solution may help. Thus, for example, when MnO_2, Fe_2O_3, etc. are boiled with conc. HCl for a long time a dark-coloured solution results, which, on dilution and subsequent boiling, gives clear solution. Again potassium arsenate or potassium antimonate on treatment with hydrochloric acid does not readily go in solution but on dilution followed by boiling a clear solution is obtained. In some cases, while trying to dissolve the substance in conc. HCl by boiling, chlorine gas may be evolved. As for example, substance containing MnO_2 when boiled with conc. HCl,—chlorine is evolved. In any case, should chlorine be evolved, boiling should be continued till the chlorine evolution ceases.

4. If a precipitate appears here, it may contain $PbCl_2$. The formation of the precipitate is helped by dilution.

5. If the preliminary tests indicate the presence of Hg_2Cl_2, Hg_2Br_2 (white); Hg_2I_2 (green); HgS (scarlet or black); Cu_2S (black); As_2S_2 (brick red); As_2S_3 (yellow); NiS, CoS (black); SnS_2 (golden yellow); Sb_2O_4, Sb_2O_5 (white); the *aqua regia* treatment should be adopted to get them in solution; otherwise

this step should be omitted and the residue obtained after the treatment with HCl should be regarded *insoluble*.

In order to avoid troubles and complications, it is advisable to analyse each solution (extract) separately. The water extract even in absence of silver group (or from which silver group has been removed by adding HCl) should not be mixed with HCl extract, as it may cause precipitation by double decomposition occurring between the substances present in the extracts. Take for an example, when Na_2SO_4 solution in water is mixed with solution of $BaCO_3$ in HCl, a precipitation of $BaSO_4$ occurs. Besides, each solution may contain only one substance, which may prove helpful while suggesting a probable composition of the sample analysed.

6. There are some substances, which resist all the methods so far described for bringing them in solution in order to detect them in the wet way. These substances are called insoluble. The insoluble substances may be attacked either by the 'General method' or by the 'Special methods', whichever be advantageous.

General Scheme for the Separation of Metals into Groups

Before entering into the actual procedure the student must note the following relevant points:

1. Analysis should be carried out with a small quantity (0·5 – 1 gm.) of the substance, because with a large quantity of the substance, the ppt. will be so bulky that difficulties will be encountered in filtering, washing and finally dissolving them.

2. All precipitates, unless otherwise stated, must be washed to remove adhering solution and the first washing must be added to the solution from which the precipitate has been filtered.

3. If the volume of the solution at any stage of anlysis becomes too large it must be reduced to a small volume by evaporation.

4. The conditions or precipitation should be strictly followed.

5. The group reagent must be added in the proper order. A group reagent separates a particular group from groups (or group) that follow but not from the group (or groups) that

GENERAL GROUP SEPARATION

After preparing the solution (of the sample supplied) according to the direction given earlier, examine the solution according to the General Group Separation Table in order to separate the metals into different groups.

TABLE 2

General Group Separation Table

To the cold solution of the substance in distilled water add a few drops of dil. HCl. If any precipitate appears go on adding dil. HCl till the precipitation is complete. Boil, cool and filter.[1]

<table>
<tr>
<td rowspan="2">Residue: White. Group I present May be AgCl, $PbCl_2$, Hg_2Cl_2. Examinne according to the table of Group I.</td>
<td colspan="2">Filtrate: Dilute the solution with equal volume of water, if it be highly acidic; heat to boiling and pass in H_2S till saturation[2]. If any precipitate appears, filter, take a little of the filtrate; dilute with equal volume of water. Heat to boiling and again pass H_2S through it. If any precipitate appears, pass H_2S through the whole of the filtrate after diluting it with equal volume of water and subsequent heating to boiling. Filter, collect all the ppt. together; repeat the process till no more precipitation occurs.
Alternatively: Make the filtrate from Group I (or HCl solution of the sample as the case may be) just alkaline (test with litmus) by adding ammonia dropwise, neglect any precipitation. And 1 c.c. 6N HCl (bench acid) per 20 c.c. of the solution Heat to boiling and pass H_2S. Now dilute the volume to three times (2 c.c. water per c.c. of the solution) and pass H_2S again as before. Filter.</td>
</tr>
<tr>
<td>Residue: Coloured. Group II present. HgS, PbS, CuS (all black); Bi_2S_3 (brown or black); CdS, As_2S_3. SnS_2 (yellow); SnS (brown): Sb_2S_3, Sb_2S_5 (orange). Wash the residue several times with hot water. Transfer to a small beaker and add yellow ammonium sulphide[3]. Warm for a few minutes while stirring with a rod, cool and filter.</td>
<td>Filtrate: Boil off H_2S completely[4] (recognised by its smell). Add 10 drops of conc. HNO_3 and boil[5] again for a minute. Add about 3-4 grams[6] of NH_4Cl per 25-30 ml. of the solution and heat to boiling. Now add NH_4OH dropwise till a slight smell[7] of ammonia persists even on boiling. Boil for a minute and filter.</td>
</tr>
</table>

<table>
<tr>
<td rowspan="3"></td>
<td rowspan="3">Residue: Sulphides of Hg, Pb, Bi, Cu and Cd. <i>Group IIA present.</i> Examine according to the table of Group IIA</td>
<td colspan="2">Filtrate: May contain thio-salt of As, Sb and Sn. Acidify the filtrate with dil. HCl.</td>
<td rowspan="3">Residue: <i>Group IIIA</i>
$Fe(OH)_3$ (brown), $Al(OH)_3$ (white). $Cr(OH)_3$ (green) and sometimes $MnO(OH)_2$ (brown). Examine according to the table of Group IIIA.</td>
<td colspan="3">Filtrate: Add[8] a little more of NH_4OH, warm and pass H_2S till complete precipitation occurs. Filter.</td>
</tr>
<tr>
<td rowspan="2">If the precipitate is only white or light yellow, Group IIB absent. Reject the precipitate.</td>
<td rowspan="2">Coloured precipitate Group IIB, <i>i.e.</i>, As, Sn, Sb <i>present.</i> Examine according to the table of Group IIB.</td>
<td rowspan="2">Residue: <i>Group IIIB present.</i> ZnS (white), MnS (Flesh coloured), NiS and CoS (both black). Examine according to the table of Group IIIB.</td>
<td colspan="2">Filtrate[9]: Boil off H_2S. Evaporate to about $\frac{1}{4}$th of its bulk. Filter off any solid that separates out. Add NH_4OH to the filtered solution till it smells of ammonia and then an excess of a freshly prepared saturated solution (about 15 c.c.) of $(NH_4)_2CO_3$; warm[10], don't boil and allow to stand[11] at lest for 10-15 minutes. Filter.</td>
</tr>
<tr>
<td>Residue: White. <i>Group IV present.</i> $BaCO_3$, $SrCO_3$, $CaCO_3$. (all white). Examine according to the table of Gr. IV.</td>
<td>Filtrate[12]: Divide the filtrate into two unequal parts:
To the larger part add Na_2HPO_4 solution. Shake well, scratch and then allow to stand. A white crystalline ppt. indicates the presence of Mg.
Evaporate the smaller portion to dryness in a fume chamber; ignite to remove all ammonium salts by volatilistion. If any residue, <i>Group V present.</i> Examine according to the table of Group V.</td>
</tr>
</table>

precedes it. Thus when metals of different groups are present in the same solution a group reagent will not only precipitate metals of the particular group but also usually those of the groups (or group) that precede it, if not separated earlier.

Notes on Table 2

1. If the original substance is completely or partly soluble in water, examine the water extract from Group 1. If, on the other hand, the original substance is insoluble in water but completely soluble in HCl, evidently no silver or mercurous salt is present. Lead when present often goes in solution in HCl while hot, but $PbCl_2$ is precipitated on cooling the solution. Part of the lead passes into solution and is precipitated in Group II by H_2S as PbS. Sometimes a precipitate may appear on the addition of hydrochloric acid to water extract even when Group I metals are absent. This precipitation may occur when:

(*a*) Concentrated solution of certain chlorides, *e.g.*, NaCl, $BaCl_2$ may give a white ppt., on the addition of hydrochloric acid due to common ion effect. This ppt., however, disappears on dilution with water.

(*b*) Aqueous solution containing Sb, Sn and Bi not containing free HCl may give rise to a ppt., on dilution with water. This precipitate is due to formation of oxy-chloride, which, however, dissolves on addition of excess of HCl.

(*c*) Aqueous solution of slicates may yield a white gelatinous ppt. of silicic acid on the addition of HCl. The ppt. does not go in solution on addition of excess of the acid.

(*d*) Aqueous solution containing thio-salts of As, Sb and Sn yields the ppt. of respective sulphides (all coloured), when the solution is acidified with dilute HCl. In such a case examine the precipitated sulphides according to the table of Group II.

(*e*) White colloidal sulphur separates out on the addition of dilute HCl to water solution of a thiosulphate.

(*f*) Addition of HCl (particularly if it is concentrated) to an aqueous solution of borate may give rise to a white ppt. of boric acid (only partial precipitation may occur here).

2. If any ppt. appears on passing H_2S through a little of this solution, pass H_2S through the bulk of the solution. If there is no precipitate, don't pass H_2S through the main bulk but boil the solution with a few drops of conc. HNO_3

and proceed as usual from Group IIIA of the General Group Separation Table. The trouble of removing H_2S from the solution may thus be avoided, if the second group elements are absent. *In order to have the best result with H_2S, the acidity of the solution is to be adjusted at* 0·25—0·3 (*M*). If the hydrogen ion concentration of the solution is much higher than this value, CdS is not precipitated and sulphides of lead and tin are incompletely precipitated. If, on the other hand, the hydrogen ion concentration falls below this value, oxy-salts of Bi, Sb and Sn are precipitated. Besides, Zn, Ni and Co are precipitated as sulphides by H_2S in such low acid concentration. Moreover, if the acidity be not quite high, *i.e.*, of the order of 3 to 4 (N), sulphides like As_2S_3 are not precipitated and tend to form a stable sol. For all practical purposes, make the filtrate from Group I distinctly acidic, heat to boiling and pass H_2S. Filter; dilute the filtrate with water and pass H_2S. Repeat the process till the precipitation is complete. Or, follow the alternative method as detailed in Table 2.

If an oxidising agent (*e.g.*, nitrite, chromate, arsenate and ferric salts) is present, reduce it before passing H_2S through the solution. Because *H_2S is first oxidised by oxidising agent and as a result gradual separation of fine white sulphur takes place.* This delays the precipitation of sulphides of metals. Moreover, sulphur is mostly in the colloidal state and passes through pores of the filter paper. Ferric salts, for example, is reduced by H_2S into ferrous salt and sulphur is precipitated.

$$2FeCl_3+H_2S=2FeCl_2+2HCl+S.$$

(*i*) Sulphites, which if present, interferes with the precipitation of sulphide (by the passage of H_2S) and are however decomposed by boiling the solution with concentrated HCl.

(*ii*) In the case of nitrates the solution should be boiled with an excess of conc. HCl and evaporated almost to dryness till no more fumes of nitrogen oxides are evolved.

(*iii*) Nitrites also are decomposed by boiling with excess of conc. HCl. Last traces of nitrous acid should be removed by boiling with a little urea.

$$2HNO_2+CO(NH_2)_2=2N_2+CO_2+3H_2O.$$

(*iv*) Chromates, arsenates and ferric salts are reduced by boiling the solution with SO_2-water (sulphurous acid). Note that ferric salts are reduced in only very weak acid medium by SO_2. Add sulphurous acid to the solution til the solution distinctly smells of it. Boil off the excess of sulphur dioxide. It may so happen sometimes that a white ppt. appears on boiling with SO_2-water. On such an occasion filter off the ppt. Examine the filtrate thus obtained from Group II of the General Group Separation Table. Wash the residue with water; perform flame test with a little of it as this may give an indication of the metallic radical (or radicals) present. Treat the residue as insoluble (*see* the Treatment of Insoluble Substances). The ppt. is due to the conversion of compounds of Pb, Ba, Sr and Ca (present singly or in mixture) into their sulphates.

3. To facilitate analysis the metals of this group (*i.e.*, Group II) are again sub-divided into A and B sub-group depending upon the solubility of sulphides of this group in yellow ammonium sulphide. Sulphides of arsenic, antimony and tin are soluble in yellow ammonium sulphide solution forming thio-salts. The solution thus obtained, if acidified with dil. HCl, the higher sulphides are precipitated and the excess yellow ammonium sulphide is decomposed. These basic radicals form Group IIB: while the metals, whose sulphides are insoluble in yellow ammonium sulphide, form Group IIA.

The reaction, for example, between As_2S_3 and yellow ammonium sulphide, which is a poly-sulphide and also an oxidising agent is shown below:

$As_2S_3+3(NH_4)_2S+2S=2(NH_4)_3AsS_4$ (ammonium thioarsenate).

Similarly, with Sb and Sn, $(NH_4)_3SbS_4$ ammonium thioantimonate, $(NH_4)_2SnS_3$ ammonium thiostannate are formed respectively.

The reactions on acidification of thio-salt solution are:

$$2(NH_4)_3AsS_4+6HCl = As_2S_5+6NH_4Cl+3H_2S$$
$$2(NH_4)_3SbS_4+6HCl = Sb_2S_5+6NH_4Cl+3H_2S$$
$$(NH_4)_2SnS_3+2HCl = SnS_2+2NH_4Cl+H_2S.$$

It is to be remembered that HgS and CuS are slightly soluble in yellow ammonium sulphide and they are precipitated from their solution in yellow ammonium sulphide on acidification. Of these two sulphides, copper sulphide appears brownish red and hence may be mistaken for Sb_2S_3 but mercury sulphide is black and no such difficulty arises in this case. Besides, as has been already stated yellow ammonium sulphide is decomposed on acidification and consequently much sulphur (white or light yellow) is deposited.

4. *H_2S should be boiled off from the filtrate of Group II*; otherwise addition of ammonium hydroxide leads to the formation of ammonium sulphide, which causes the metals of IIIB to be precipitated as sulphides. Hence addition of ammonia in such a case not only causes the precipitation of hydroxides of Fe, Al and Cr but also sulphides of Group IIIB metals.

5. Ferrous ion is incompletely precipitated by NH_4OH. Hence ferrous ion, if originally present or formed by the action of sulphurous acid (when sulphurous acid is used for reduction) or by the action of H_2S (if H_2S is passed through the main bulk of the solution to have the precipitation of Group II metals) should be oxidised to ferric ion by boiling with a few drops of concentrated HNO_3 or bromine water.

6. Ammonium chloride separates the metals of Group IIIA from those of succeeding groups, since only ammonium hydroxide, if added, not only hydroxides of Fe, Al and Cr but also those of Zn, Mn, Ni, Co and Mg are precipitated. Addition of NH_4Cl affects the ionisation of NH_4OH, it greatly reduces the hydroxyl ion concentration (common ion effect and buffer action) so much so that only the hydroxides of Fe, Al and Cr are precipitated. Presence of sufficient amount of NH_4Cl. therefore, prevents a good many metals from being precipitated here on addition of NH_4OH.

If the presence of borate, fluoride, phosphate and silicate be detected, they must be removed before proceeding with the analysis from Group IIIA of the General Separation Table. The above named four radicals are called 'interfering' acid radicals, as borate, fluoride, phosphate, silicate of the metals of Group IIIA, IIIB, IV and of Mg are precipitated with the hydroxides of metals of Group IIIA on rendering the solution alkaline by addition of NH_4OH in Group IIIA. This difficulty, however, does not arise so long as the solution remains acidic. Hence the necessity of their removal after the separation of metals of Group II [*see* the 'Removal of Interfering Acids'].

7. Note that the addition of *much excess of ammonia should be avoided*. As excess ammonia may dissolve $Cr(OH)_3$ and $Al(OH)_3$. The hydroxides are, however, precipitated by boiling off excess of ammonia. Ammonium hydroxide should be added to the solution while hot as this helps to coagulate the ppt. Manganese, if present, is often precipitated as higher hydrated oxides in Group IIIA along with hydroxides of that group. This precipitate of manganese compound is of the same colour (brownish) as that of $Fe(OH)_3$. Hence Group IIIA, ppt. must be looked for manganese also.

8. In passing to Group IIIB, the filtrate from Group IIIA should not be treated with much excess of H_2S, as this causes NiS to pass into solution in the colloidal state. Moreover, the whole filtrate from Group IIIA should not be immediately treated with NH_4OH and H_2S. Test a little of the filtrate with ammonium hydroxide and H_2S. If any precipitate, treat the whole of the filtrate with NH_4OH and H_2S in the manner stated in the General Separation Table, otherwise omit the step and examine the filtrate directly for Group IV.

9. The filtrate from Group IIIB should be acidified (slight acidic) with acetic acid immediately after filtration and *concentrcted to about ¼th of its bulk*. Acidification of the filtrate with acetic acid followed by boiling has many-fold advantages: (*i*) Any NiS that has passed into solution in the colloidal form (which is indicated by brown or dark colour of the filtrate) and has thus escaped precipitation in IIIB is coagulated. It is filtered off. This ppt. may be added to the ppt. of IIIB and treated accordingly or may here be tested separately for Ni. (*ii*) It causes removal of H_2S from the solution and thus prevents the oxidation of ammonium sulphide by air to ammonium sulphate. Ammonium sulphate, if formed, causes precipitation of metals of Group IV as insoluble sulphate. (*iii*) Besides, acidification prevents the absorption of CO_2 from atmosphere by ammonia and thus the formation of ammonium carbonate is avoided.

10. *The medium must be kept ammoniacal. But it should be noted that ammonium chloride, if present in excess in the solution, interferes with the precipitation of Group IV metals as carbonates.* Hence it should be removed according to the

direction given in the General Separation Table. The laboratory reagent—ammonium carbonate though contains a fair amount of ammonium bicarbonate, the formation of soluble bicarbonates of alkaline earth metals is prevented in ammonical medium. Since the presence of excess of ammonia destroys bicarbonate by converting it into carbonate. Note that after the addition of ammonium carbonate the solution should be warmed but not boiled. Because the reaction $MCO_3+2NH_4Cl \rightleftharpoons MCl_2+(NH_4)_2CO_3$ (where M is Ca, Ba, Sr) is reversible, boiling volatilises $(NH_4)_2CO_3$; hence the reaction proceeds from the left to right and consequently precipitated carbonate goes in solution. But warming is necessary as the filtering property of the precipitate is improved thereby. Moreover, bicarbonate, if formed at all, undergoes decomposition on warming.

11. The solution to which the Group IV reagents have been added should be allowed to stand at least for a few minutes, since precipitation of Group IV metals takes time.

12. The Group IV metals may be partially precipitated or may even escape precipitation due to several factors as discussed above. The filtrate from Group IV should, therefore, be treated with 2 c.c. each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ solution, the resultant solution is heated to boiling and allowed to stand for at least five minutes. If any precipitate appears, filter it off. (This ensures complete removal of Group IV metals.) If this is not done the filtrate from Group IV on being treated with di-sodium phosphate may give a ppt. and this often misleads one to suspect the presence of magnesium even when no magnesium is supplied.

Classification of Metallic Ions into Different Groups

It is quite evident from the Table 2 described in pages 38-39 that for purpose of systematic qualitative analysis the metallic ions have been classified into different analytical groups with the help of certain reagents known as group reagents. This classification is based on the varying solubilities of chlorides, sulphides, hydroxides and carbonates. Thus, as has already been stated in Table 2, that dil. HCl, if added in slight excess, to a solution containing common metallic ions chlorides of

Ag. Pb and mercurous mercury only are precipitated; these chlorides not being soluble in cold and dil. HCl. These three metallic ions together form Gr. I or what is known as silver group. Similarly, by employing suitable reagents, the remaining metallic ions have been separated into several different groups. The following table gives in short a summary of the scheme of this divisions as detailed in Table 2.

Metallic ions	Group	Group reagent	Precipitate obtained	Special features
Ag^+, Pb^{++}, Hg_2^{++}	I (Silver group).	Dil. HCl	AgCl, $PbCl_2$. Hg_2Cl_2.	Chlorides insoluble in cold dilute HCl.
Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}; As^{+++}, Sb^{+++}, Sn^{++++}, Sn^{++}	II (Copper and Arsenic group).	H_2S in presence of dil. HCl.	HgS, PbS, Bi_2S_3,CuS, CdS; As_2S_3,Sb_2S_3, SnS,SnS_2.	Sulphides insoluble in dil. HCl.
Fe^{+++}, Al^{+++}, Cr^{+++}	IIIA (Iron group).	NH_4OH in presence of NH_4Cl.	$Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$.	Hydroxides are precipitated by NH_4OH in presence of NH_4Cl.
Zn^{++}, Mn^{++}, Ni^{++}, Co^{++}	IIIB (Zinc group).	H_2S in presence of NH_4OH and NH_4Cl.	ZnS, MnS, NiS, CoS	Sulphides soluble in acid but precipitated in alkaline condition.
Ca^{++}, Ba^{++}, Sr^{++}	IV (Calcium group).	$(NH_4)_2CO_3$ in presence of NH_4OH and NH_4Cl.	$CaCO_3$, $BaCO_3$, $SrCO_3$.	Carbonates are precipitated by $(NH_4)_2CO_3$ in presence of NH_4Cl.
Na^+, K^+, *NH_4^+,Mg^{++}	V (Alkali group).	No group reagent.	—	Na_2HPO_4 in presenc of NH_4Cl and NH_4OH precipitates out Mg^{++} as $Mg(NH_4)PO_4$, all salts of other metallic ions of this group being soluble.

*Though NH_4^+ is included into the 5th group, the test for it (NH_4^+) should, however, be carried out at the beginning of *analysis* with a portion of the original sample. *See* pages 21, 72, 73.

Principle of Group Separation

From the principle of solubility product we know that when the product of the concentrations of ions of a sparingly soluble salt is greater than its solubility product, precipitation will occur. Thus in Gr. I we add HCl, which dissociates into H^+ and Cl^- ions. The concentration of Cl^- ions becomes sufficient to exceed the solubility product of AgCl, $PbCl_2$ and Hg_2Cl_2 but not sufficient to exceed the solubility product of the chlorides of metals of subsequent groups. Thus $PbCl_2$, Hg_2Cl_2 and AgCl only are precipitated in Gr. I.

In Gr. II we pass H_2S through solution acidified with HCl. Sulphuretted hydrogen in aqueous solution behaves as a weak acid. Consequently, its degree of dissociation is very small. Moreover, in presence of HCl, which dissociates into H^+ and Cl^- ions the dissociation of sulphuretted hydrogen is further depressed due to *common ion effect* (H^+ ion being common). Hence under the condition only a very low concentration of sulphide ion is attained. But even with this low value of sulphide ion (S'') concentration the solubility product of the sulphides of Gr. II metals are exceeded and these are therefore almost completely precipitated. Whereas the solubility product of the sulphides of metals of subsequent groups are not exceeded under the condition. Thus, sulphides of Zn, Mn Ni, Co, etc. are not precipitated but CuS, PbS etc. are precipitated in Group II.

In order to precipitate out the Gr. IIIB metals as sulphides a comparatively high concentration of sulphide ion is necessary, which may be achieved by reducing hydrogen ion concentration of the solution. In Gr. IIIB, H_2S is passed in presence of NH_4OH, which dissociates into NH_4^+ and OH^- ions. The latter ions by reacting with H^+ ions derived from the dissociation of H_2S remove it (H^+ ions) from the system. Consequently, according to the principle of chemical equilibrium, more and more H_2S will now be dissociated, which will result into an increased value of the concentration of sulphide ion. Under the circumstances, the solubility product of the sulphides of Gr. IIIB (which is greater than those of the sulphides of Gr. II) will be exceeded and hence Zn, Mn, Ni and Co will be precipitated as their sulphides in Gr. IIIB.

The metals of Gr. IIIA are precipitated as hydroxides by adding NH_4Cl and NH_4OH to the solution. The latter being a weak base dissociates to a small extent into NH_4^+ and $(OH)^-$ ions. In presence of NH_4Cl this dissociation is further depressed due to common ion effect (NH_4^+ ion being common) yielding thereby only a very low concentration of $(OH)^-$ ions. This low value of $(OH)^-$ ion concentration is sufficient to exceed the solubility product of the hydroxide of Gr. IIIA metals but insufficient to exceed the same for the hydroxides of Grs. IIIB, IV, and V metals.

In Gr. IV we use NH_4OH and $(NH_4)_2CO_3$. By using the lowest limit of concentration of metal ions as 10^{-4} (M), the product of the ionic concentration (of the carbonate and metal ion) becomes approximately $1{\cdot}6 \times 10^{-4}$. This value is less than the solubility product of carbonate of magnesium but greater than the solubility product of carbonates of Ba, Sr and Ca. That is why the carbonates of Ba, Sr and Ca are precipitated in Gr. IV but magnesium still remains in solution.

Magnesium ions remaining in solution are precipitated out by addition of disodium hydrogen phosphate, Na_2HPO_4 [as a white crystalline ppt. of $Mg(NH_4)PO_4,6H_2O$].

Removal of Interfering Acids

(Boric, Hydrofluoric, Silicic and Phosphoric acids)

Under the notes on General Separation Table it has already been stated that the presence of the above four acids necessitates the modification of the usual scheme of analysis after Group II for the separation of basic radicals into different groups.

Borates and fluorides

Evaporate in a basin the filtrate from Group II to dryness. Treat the residue with conc. HCl; evaporate again almost to dryness. Repeat the evaporation with conc. HCl till the residue gives no test* for borate or fluoride (or both) as the case may be. Take up the residue with dil. HCl by warming if necessary. Filter off any residue. Boil the resulting solution with a few drops of conc. HNO_3. Examine the solution from Group IIIA onwards according to the usual scheme of analysis. Boric acid volatilises in the steam and HF volatilises with HCl.

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*Note that the removal of these interfering acids is often complete, if the evaporation with conc. HCl be carried out twice or thrice.

N.B. In absence of fluoride, borate may easily be removed by repeated evaporation of the filtrate from Group II to dryness with a mixture of conc. HCl and methyl alcohol. In this process volatile methyl borate is formed and it volatilises away.

Silicates

Treat with conc. HCl, the residue obtained by evaporation of the filtrate from Group II and evaporate to dryness with constant stirring. Repeat the operation with a further quantity of conc. HCl. Bake the residue thus obtained on an asbestos board or sand bath for at least 15 minutes. Cool, extract with dilute HCl (warming, if necessary). Filter off the residue. Boil the filtrate with a few drops of conc. HNO_3 and examine the filtrate from Group IIIA onwards.

Note that the silicates that are soluble in water, acids or *aqua regia* are always decomposed, if the above process of repeated evaporation with conc. HCl is resorted to.

[In case of silicates not decomposable by HCl, fuse the solid with Na_2CO_3 (1: 4) in a nickel crucible. Extract with hot water after cooling; add conc. HCl in excess and evaporate to dryness. Repeat the process of evaporation by moistening the residue with conc. HCl and bake the evaporated mass for at least 15 minutes on an asbestos board or a sand bath. Cool the mass and extract with dil. HCl by warming, if necessary. Filter. Examine the filtrate for cations according to the General Group Separation Table.

Insoluble silicates require this method of treatment.]

N.B. (*i*) Treatment with HCl followed by baking converts silicates into an insoluble form of SiO_2, which is removed by filtration.

(*ii*) The silica residue should be examined for Al_2O_3, Fe_2O_3 and Cr_2O_3, since the above process of removal of silicates often makes Al_2O_3, Fe_2O_3 and Cr_2O_3 insoluble (as a result of baking), which remains on the filter paper together with SiO_2. Fuse silica residue with $KHSO_4$. Cool, extract with hot dilute HCl; filter and examine the filtrate for iron, aluminium and chromium.

(*iii*) If the metallic radicals of Group IV are not present it is better to decompose the borates, fluorides and silicates by using conc. H_2SO_4 instead of HCl. The residue, after cooling, is extracted with dil. HCl and filtered. The filtrate is then boiled with HNO_3 as usual and made ready for analysis from Group IIIA onwards.

The H_2SO_4 treatment may be resorted to even in presence of Group IV metals; but in that case the residue obtained after extracting the fused mass with dil. HCl should be treated according to the 'Treatment of Insoluble Substances', since the Group IV metals are converted into insoluble sulphates in this process. The HCl extract of the fused mass is made ready for analysis from Group IIIA onwards after boiling it with a few drops of conc. HNO_3.

Phosphoric acid:

The principle for the separation of phosphates by the method described below (pages 51-52) may be summarised as follows:

(*i*) The phosphates of the metals of $(NH_4)_2S$ Group (IIIB), $(NH_4)_2CO_3$ Group (IV) and Mg are soluble in acetic acid in the presence of *excess* of acetate ions whereas $FePO_4$, $AlPO_4$ and to a lesser extent $CrPO_4$ are insoluble in the said medium.

(*ii*) If to a solution containing Fe, Al and Cr an acetate solution be added, the acetates of these metals are produced. If this be diluted and boiled Fe and Al are almost completely precipitated out from the solution as basic acetate, but the precipitation of Cr, however, depends upon the relative quantities of Fe and Al present in the solution.

(*iii*) So, if Fe^{+++} ions (unless there is already present in sufficient quantity to combine with whole of the PO_4''' ions) are introduced, the excess of PO_4''' ions are removed as insoluble $FePO_4$ from the medium buffered by acetic acid and an alkali acetate. As soon as all the PO_4''' ions are removed a little excess of Fe^{+3} ions react with acetate ions to give ferric acetate, which (on boiling gives basic Fe-acetate) has a red colour and hence the appearance of *red colour* indicates an excess of ferric ions. The addition of $FeCl_3$ is to be stopped at this stage.

Advantages of using $FeCl_3$

(*i*) It is easy to detect the presence of iron in the filtrate from Group II.

(*ii*) $FePO_4$ is the least soluble phosphate that may be precipitated in the acetic acid medium.

(*iii*) The slight excess of ferric ions that have been added can be easily removed, because the ferric acetate formed hydrolyses on dilution and boiling to basic ferric acetate, which is precipitated.

Procedure for removal of Phosphoric acid

Before entering into actual separation, perform the tests for phosphate and iron :

Boil off H_2S from the filtrate of Group II. Add a few drops of conc. HNO_3 to it and boil again.

Add a little of this solution to an excess of ammonium molybdate solution taken in a test-tube; warm up to 40°, if necessary. A *canary yellow precipitate* confirms *Phosphate*.

Test another small portion of the solution with $K_4[Fe(CN)_6]$ or NH_4CNS solution. Formation of a deep-blue colour (or ppt.) with $K_4[Fe(CN)_6]$ and a *blood-red colour* with NH_4CNS confirm *Iron*.

To the main portion of the solution (15-20 c.c.) add about 2 gms. of NH_4Cl. Heat to boiling. Add dil. NH_4OH dropwise till a *slight* permanent turbidity occurs. Now boil[1] a little and dilute[2] (to about 30 c.c.). Add 2-3 c.c. of dilute acetic acid and about 20 c.c. of a saturated solution of ammonium acetate[3]. Boil and filter hot.

<table>
<tr><td rowspan="4">Residue A:
A mixture of phosphates and basic acetates of Fe, Al and Cr.
Examine according to the table of Gr. IIIA.</td><td colspan="4">Filtrate A:
If the filtrate is not red[4] in colour, add freshly prepared neutral $FeCl_3$ solution dropwise stirring the hot mixture all the time, till the solution acquires the cream colour of a light tea. Boil for a few minutes and filter hot.</td></tr>
<tr><td rowspan="3">Residue B:
$FePO_4$ and basic iron acetate.
Reject it.</td><td colspan="3">Filtrate B:
The filtrate is often colourless (but may sometimes be coloured as the sample may contain compounds of Ni, Co and Mn). Test a little of the filtrate with a drop of $FeCl_3$. If it turns red, phosphate has been completely removed. Proceed from as detailed under <i>filtrate C</i> below. But if a yellow precipitate appears on addition of $FeCl_3$, phosphate has not been completely removed. In the latter case, continue addition of $FeCl_3$ to the main bulk of the <i>hot</i> filtrate till it assumes the cream colour of a light tea. Boil and filter.</td></tr>
<tr><td rowspan="2">Residue C:
Reject it.</td><td colspan="2">Filtrate C:
Heat to boiling. Add NH_4OH in slight excess and filter.</td></tr>
<tr><td>Residue D:
Reject it.</td><td>Filtrate D:
Examine according to the 'General Group Separation Table' from Group IIIB onwards.</td></tr>
</table>

A portion of the residue D should be tested accorrding to Table 7 for Manganese (as it may get precipitated here along with Fe^{+3}).

Notes on Phosphate separation

1. If no precipitate appears here even on *boiling off ammonia* the substance consists of Na, K and NH_4^+ only. In such a case further analysis is unnecessary. Test for Na, K and NH_4^+ in the original solution. If, on the other hand, a precipitate appears on boiling off ammonia, proceed as directed above.

2. The solution should be diluted as otherwise phosphate of **Ba**, Ca and Sr may come down as precipitate in the next stage, when acetate ions are introduced.

3. Formation of a ppt. on addition of acetic acid and an acetate indicates the presence of Fe, Al and Cr in the original sample.

4. Production of red colour, on addition of acetic acid and ammonium acetate on the other hand, indicates that an excess of the required minimum of iron must have been present in the sample. In such a case don't add $FeCl_3$ but add a dilute solution of ammonium phosphate drop by drop till the solution acquires the cream colour of a light tea. Boil for a minute or two and filter. Reject the ppt. Test a little of the filtrate as usual to see if phosphate has been completely removed or not. If the filtrate is free from phosphate, examine the main bulk of the filtrate from Group IIIB onwards according to the General Group Separation Table.

Note that on such an occasion an alternative but perhaps easier method of attaining the same objective is: Don't add $FeCl_3$. Dilute the solution considerably, boil for 2-3 minutes and filter hot.

<table>
<tr><td rowspan="2">Residue:
Reject it. It consists of $FePO_4$ and basic ferric acetate.</td><td colspan="2">Filtrate:
Concentrate to a small volume (about 20 c.c.); add 0·5 gm of NH_4Cl and then NH_4OH in slight excess. Filter, if required.</td></tr>
<tr><td>If any <i>residue</i>, examine for Al, Cr and Mn (if not previously tested for).</td><td>Filtrate:
Examine for cations from Gr. IIIB onwards according to usual scheme.</td></tr>
</table>

TABLE 3

Analysis of Group I Metals (Silver Group)

The ppt. obtained by adding dil. HCl dropwise to the original solution may consist of $PbCl_2$, AgCl and Hg_2Cl_2. Filter. Neglect the filtrate, if metal or metals of only this group be supplied; otherwise preserve it for analysis of metals of succeeding groups. Examine the ppt. in the following way for metals of Group I.

Wash the ppt. on the filter paper 2 or 3 times with a little cold water and reject the washings. Transfer the ppt. in a beaker, and boil with much (about 20 c.c.) water and filter hot.

<table>
<tr>
<td colspan="2">**Residue:** Wash the residue thoroughly with hot water, this ensures complete removal of lead. To the residue on the filter paper add about 10 c.c. of warm NH_4OH (6M) and collect the filtrate.</td>
<td rowspan="2">**Filtrate:** (*i*) Allow the filtrate to cool. If the solution be sufficiently concentrated, white crystalline ppt. of $PbCl_2$ appears. The ppt. however dissolves on boiling but reappears on cooling.
(*ii*) Acidify a portion of the filtrate with acetic acid (6M); add K_2CrO_4 solution. A yellow ppt. of lead chromate confirms *Lead*.
(*ii*) To a portion of the nearly cooled filtrate add KI solution. A yellow ppt. soluble on boiling but re-appears as golden yellow crystals on cooling confirms *Lead*.
(*iv*) To another portion of the filtrate add dil. H_2SO_4 and alcohol. A white ppt. soluble in a strong solution of ammonium acetate confirms *Lead*.</td>
</tr>
<tr>
<td>**Residue***: The residue on the filter paper turns black. Treat the residue with *aqua regia* and evaporate to dryness. Extract the mass with water. Decant off the clear liquid (if necessary) from the top.
(*i*) To a portion of this clear solution add $SnCl_2$ solution.
A white ppt. (of Hg_2Cl_2) or a grey ppt. (of Hg) confirms *Mercury*.
(*ii*) Dip a clean copper foil or copper coin in the remaining portion of the solution—a grey or white deposit of metallic mercury on copper confirms *Mercury*.</td>
<td>**Filtrate:** Divide it into *two* parts:
(*i*) Acidify one part with dil. HNO_3. Test with litmus. White ppt. confirms *Silver*.
(*ii*) To the other part add a few drops of KI solution—a yellow ppt. of AgI confirms *Silver*.</td>
</tr>
</table>

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*The residue may be tested for mercury in the following way: Dissolve the residue in hot conc. HCl and bromine water. Boil off the excess of bromine and ultimately treat the solution thus obtained with $SnCl_2$ solution as usual, when a white or a grey ppt. confirms *Mercury* and thus the *aqua regia* treatment may be avoided, if and when required.

Principles of analysis of metals of Group I

Lead, silver and mercurous mercury ions are thrown out of the solution as respective chlorides upon addition of dil. HCl to a solution containing the above ions. Of the chlorides thus precipitated, Hg_2Cl_2 and AgCl are insoluble in boiling water while $PbCl_2$ is soluble in boiling water.

Lead is, therefore, looked for in the filtrate from 'boiling water' treatment. The confirmatory tests for lead involve the precipitation of Pb^{++} ion from the solution as (*i*) lead iodide, (*ii*) lead sulphate, (*iii*) lead chromate, etc.

$$PbCl_2+2KI = PbI_2+2KCl$$
$$PbCl_2+H_2SO_4 = PbSO_4+2HCl$$

Similar reaction occurs between Pb^{++} ion and K_2CrO_4.

The residue after the removal of $PbCl_2$ by 'boiling water' treatment consists of Hg_2Cl_2—AgCl mixture. AgCl goes in solution in NH_4OH forming the complex salt $[Ag(NH_3)_2]Cl$. Treatment of the residue with NH_4OH, therefore, removes AgCl. Confirmatory test for silver ions are then carried out with this solution. The complex silver ammonia ion on reaction with KI yields a pale yellow ppt. of AgI. The complex ion is also decomposed by dil. HNO_3. Addition of HNO_3, therefore, causes precipitation of AgCl from the solution.

$$AgCl+2NH_3 = [Ag(NH_3)_2]Cl$$
$$[Ag(NH_3)_2]Cl+KI+2H_2O = AgI+2NH_4OH+KCl$$
$$[Ag(NH_3)_2]Cl+2HNO_3 = AgCl+2NH_4NO_3.$$

Hg_2Cl_2 on reaction with NH_4OH solution yields a mixture of amino-mercuric chloride and finely divided mercury; the colour of the latter being black the whole mass appears black.

$$Hg_2Cl_2+2NH_4OH = Hg+NH_2HgCl+NH_4Cl+2H_2O$$

Aqua regia dissolves the black mixture.

[For chemistry of conclusive tests for mercury *see* Principles of Analysis of Metals of Group IIA.]

TABLE 4

Separation of Group IIA and Group IIB

Gr. IIA (Copper group): Pb. Cu, Hg (ic), Bi and Cd
Gr. IIB (Arsenic group): As, Sb and Sn.

Filter the ppt. obtained by repeated passage of H_2S through the solution. Collect all the ppt. together. Reserve the filtrate for analysis of metals of succeeding groups. But if metal or metals of only this group be supplied neglect the filtrate. Treat the collected ppt. in the following way:

Wash the ppt. obtained in Group II several times with hot water; transfer it into a small beaker. Add about 10 c.c. of yellow ammonium sulphide solution. Warm the mixture for a few minutes while stirring with a rod. Dilute with water and filter.

Residue : Gr. IIA present. Examine according to the table of Group IIA (Table 5).	**Filtrate:** May contain thiosalts of As, Sb and Sn. Acidify with dil. HCl.	
	If a *coloured ppt.* comes down on acidification, Group IIB, *i.e.*, As, Sb and Sn present. Examine the ppt. according to the table of Group IIB (Table 6).	If, on the other hand, the ppt. is *white* or *very light yellow* in colour, Group IIB is absent. Reject the ppt., which is nothing but sulphur separated from yellow ammonium sulphide.

Principles underlying the analysis of Group IIA metals

The sulphides of the metals of this group are insoluble in yellow ammonium sulphide and hence they are left behind as residue after digestion with yellow ammonium sulphide.

On treatment of the residue with dil. HNO_3, save and except HgS, which remains insoluble, the other sulphides, namely, the sulphides of Pb, Bi, Cu and Cd go into solution as nitrates and sulphur is liberated.

$$3PbS+8HNO_3 = 3Pb(NO_3)_2+3S+2NO+4H_2O.$$

Similar reactions take place with sulphides of Bi, Cu and Cd.

The insoluble residue (*i.e.*, HgS) from HNO_3 treatment is converted into mercuric chloride by the action of *aqua regia*.

Mercury is identified in mercuric chloride solution by its reaction with $SnCl_2$ when a white ppt. of Hg_2Cl_2 or a grey ppt. of Hg is obtained.

$$3HgS+2HNO_3+6HCl = 3HgCl_2+4H_2O+2NO+3S$$
$$2HgCl_2+SnCl_2 = SnCl_4+Hg_2Cl_2$$
$$Hg_2Cl_2+SnCl_2 = 2Hg+SnCl_4$$

In another test for mercury, the displacement of mercury from its salt solution by another metal namely copper, which stands higher up in the 'electromotive series of metals' is utilised.

$$HgCl_2+Cu = Hg+CuCl_2$$

The filtrate from HNO_3 treatment contains ions of lead, bismuth, copper and cadmium from which lead is separated as insoluble $PbSO_4$. Lead is then confirmed by dissolving $PbSO_4$ into ammonium acetate solution and then precipitating out Pb^{++} ion as yellow lead chromate from acetate solution by addition of K_2CrO_4 solution.

$$PbSO_4+2CH_3COONH_4 = (CH_3COO)_2Pb+(NH_4)_2SO_4$$
$$(CH_3COO)_2Pb+K_2CrO_4 = PbCrO_4+2CH_3COOK$$

Addition of excess of NH_4OH to the solution containing Bi-, Cu- and Cd-ions causes precipitation of hydroxide of bismuth and the formation of the soluble complex ions, $[Cu(NH_3)_4]^{++}$ and $[Cd(NH_3)_4]^{++}$. In one confirmatory test for bismuth, alkali stannite solution is added to bismuth hydroxide, when the latter turns black due to separation of metallic Bi. This is due to reduction of bismuth hydroxide by alkali stannite, which is itself oxidised to alkali stannate.

$$2Bi(OH)_3+3Na_2SnO_2 = 2Bi+3Na_2SnO_3+3H_2O$$

In another test for Bi, the precipitated hydroxide is dissolved in HCl and the resulting solution is hydrolysed, when a white ppt. of oxy-salt is obtained.

$$BiCl_3+H_2O \rightleftharpoons BiOCl+2HCl$$

The filtrate from NH_4OH treatment may contain $[Cu(NH_3)_4]^{++}$ and $[Cd(NH_3)_4]^{++}$ ions. The blue colour of this filtrate indicates the presence of *copper*. Acidification of the filtrate with acetic acid results in the decomposition of the complex $[Cu(NH_3)_4]^{++}$ into Cu^{++} ion. Addition of $K_4Fe(CN)_6$

TABLE 5

Analysis of Group IIA Metals

Wash the residue[1] obtained from yellow ammonium sulphide treatment well with hot water. Puncture the filter paper and wash the residue down into the beaker with about 10-15 c.c. dil. HNO_3* (1 part conc. acid, 3 parts of water). Now boil for 2-3 minutes; cool and filter.

<table>
<tr>
<td rowspan="3">Residue[2]†: Dissolve‡ the residue in <i>aqua regia.</i> Evaporate nearly to dryness, dilute with water and filter (if necessary). Divided the filtrate into <i>two</i> parts:
(<i>i</i>) To one part add a few drops of $SnCl_2$ solution. A white or grey ppt. confirms <i>Mercury</i>(ic).
(<i>ii</i>) Dip a clean copper coin or copper turning in the remaining part of the solution. A grey deposit on the copper coin confirms <i>Mercury</i> (ic).</td>
<td colspan="3">Filtrate: Treat a little of the filtrate in a test-tube with little alcohol and dil H_2SO_4, allow to stand—a white ppt. indicates the presence of <i>Pb</i>. In such a case, add to the main balk of the filtrate about 3 c.c. alcohol and about 0·5 c.c. dil. H_2SO_4; allow it to stand for a few minutes and filter. If Pb is absent <i>omit</i> this operation.</td>
</tr>
<tr>
<td rowspan="2">Residue:
It is <i>white</i> in colour. Wash, and dissolve by boiling in conc. ammonium acetate solution. Add. dil. acetic acid and K_2CrO_4 solution. Yellow ppt. of $PbCrO_4$ confirms <i>Lead.</i></td>
<td colspan="2">Filtrate: Boil off alcohol., if previously added. Add NH_4OH solution dropwise with stirring until the filtrate reacts distinctly alkaline. Filter.</td>
</tr>
<tr>
<td>Residue: White. Wash several times with small quantity of water. Divide it into <i>two</i> parts:
(<i>i</i>) To one part add a few drops of freshly prepared alkali stannite[φ] solution; blackening of</td>
<td>Filtrate: If blue, copper is is present.
(<i>i</i>) Acidify one part of the filtrate with acetic acid and add a few drops of potassium ferrocyanide solution. A reddish-brown or chocolate red-ppt. confirms <i>Copper</i>.</td>
</tr>
</table>

	the ppt. confirms *Bismuth* (*ii*) Dissolve the other part in minimum volume of dil. HCl and pour down into a large volume of water contained in a beaker. Milkiness of water confirms *Bismuth*.	(*ii*) Discharge the blue colour of the other portion of the filtrate by adding KCN solution dropwise. Add a few drops more of KCN and pass H_2S—a yellow ppt. of CdS confirms *Cadmium*. If the filtrate is colourless copper is absent. Test directly for cadmium. Pass H_2S through the filtrate,—yellow ppt. of CdS confirms *Cadmium*.

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*The best result is achieved by heating the washed residue[1] with water and adding conc. HNO_3 dropwise till the action starts. Concentration of the acid, if be too high PbS will be oxidised to $PbSO_4$; and remain in the residue[2] of HgS, which in that case may not appear black.

† Note that the mere presence of a black residue here is no definite proof for the presence of mercury. This residue may be due to sulphur, which is coloured black by simple mechanical attachment with the sulphide other than that of mercury.

‡ See the foot-note under Table 3, page 54, *the procedure outlined there may be adopted here also with advantage.*

ϕ *Alkali stannite*: Add a dil. solution of NaOH to a solution of stanous chloride until the initial white ppt. of stannous hydroxide *just* dissolves.

solution to this acidic solution results in the formation of a chocolate coloured ppt. of $Cu_2[Fe(CN)_6]$.

$$[Cu(NH_3)_4]^{++} + 4CH_3COOH = Cu^{++} + 4CH_3COONH_4$$

$$2Cu^{++} + [Fe(CN)_6]^{-4} = Cu_2[Fe(CN)_6].$$

While testing for cadmium in presence of copper, the filtrate containing amine complexes $[Cu(NH_3)_4]^{++}$ and $[Cd(NH_3)_4]^{++}$ is treated with dil. KCN solution, when the amine complexes are converted into cyanide complexes, potassium cuprocyanide $K_3[Cu(CN)_4]$ and potassium cadmicyanide $K_2[Cd(CN)_4]$.

$$2[Cu(NH_3)_4]^{++} + 4CN^- = \underset{\text{Cuprous cyanide}}{Cu_2(CN)_2} + (CN)_2 + 8NH_3$$

$$Cu_2(CN)_2 + 6KCN = \underset{\text{Potassium cuprocyanide}}{2K_3[Cu(CN)_4]}$$

$$[Cd(NH_3)_4]^{++} + 2CN^- = Cd(CN)_2 + 4NH_3$$

$$Cd(CN)_2 + 2KCN = \underset{\text{Potassium cadmicyanide}}{K_2[Cd(CN)_4]}$$

The dissociation of the above cyanide complexes is shown by the following equations:

$$\begin{aligned}
&K_3[Cu(CN)_4] &&\rightleftharpoons 3K^+ &&+ [Cu(CN)_4]^{-3} \\
&[Cu(CN)_4]^{-3} &&\rightleftharpoons Cu^+ &&+ 4CN^- \quad \text{(secondary dissociation)} \\
&K_2[Cd(CN)_4] &&\rightleftharpoons 2K^+ &&+ [Cd(CN)_4]^{-2} \\
&[Cd(CN)_4]^{-2} &&\rightleftharpoons Cd^{++} &&+ 4CN^- \quad \text{(secondary dissociation)}
\end{aligned}$$

Of the two complexes, potassium cuprocyanide and potassium cadmicyanide the former is stable and the latter is relatively unstable. The concentration of cuprous ion arising from the secondary dissociation of $[Cu(CN)_4]^{-3}$ as shown above is not sufficient to exceed the solubility product of cuprous sulphide Cu_2S upon the passage of sulphuretted hydrogen. The cadmium complex, on the other hand, being relatively unstable as stated earlier, the concentration of Cd^{++} ion produced by secondary dissociation exceeds the solubility product of CdS upon the addition of H_2S; precipitation therefore occurs. Hence if H_2S is passed through the solution in presence of excess of KCN solution, CdS is precipitated but no copper sulphide inspite of the fact that the solubility product of copper sulphide is much smaller.

If copper is absent (which is indicated by the colour of the solution) the passage of H_2S through the filtrate containing the complex $[Cd(NH_3)_4]^{++}$ ion causes precipitation of yellow CdS.

TABLE 6

Analysis of Group IIB Metals

Wash with hot water the ppt. obtained on acidification of yellow ammonium sulphide (solution) extract and reject the washings. Transfer the ppt. into a beaker and boil gently with 10 c.c. conc. HCl for five minutes. Cool the solution; dilute with 2-3 c.c. water and filter.

Residue:	**Filtrate:**
Yellow or brown; wash it with hot water and confirm the presence of arsenic by *either* of the following tests: (*i*) Dissolve the residue in conc. HNO_3(or, conc. HCl+ a few crystals of $KClO_3$) by heating. Evaporate nearly to dryness. Dilute with water, add NH_4OH solution in excess. Filter, if necessary. Now add magnesia mixture. Cool and shake vigorously. White crystalline ppt. pf $Mg(NH_4)AsO_4$ indicates the presence of *As*. Filter, wash the ppt. to make it free from NH_4OH. Add on to the ppt. a few drops of $AgNO_3$ solution acidified with acetic acid. A brown or chocolate ppt of silver arsenate confirms *Arsenic*. (*ii*) Heat gently the residue with powdered ammonium carbonate and a little water for 2 to 3 minutes. Filter, if necessary. Acidify the resulting solution with dil. HCl—a yellow ppt. of As_2S_5, confirms the presence of *Arsenic*.	May contain $SbCl_3$, $HSbCl_4$, $SnCl_4$, H_2SnCl_6. Dilute with water and divide it into *two* portions: (*i*) Make one portion just alkaline with NH_4OH add 3-4 gms. of solid oxalic acid. Dilute with water and boil till oxalic acid is dissolved. Pass H_2S through the hot solution—an orange-yellow ppt. confirms *Antimony*. (*ii*) Add reduced iron powder to the remaining portion of the filtrate. Dilute with water. Heat for about 3 to 4 minutes. Filter, collect a little of the filtrate directly into a test tube containing $HgCl_2$ solution. A white ppt. of Hg_2Cl_2 or a grey ppt. of Hg confirms *Tin*.

Principles underlying the Analysis of Group IIB Metals

The higher sulphides of the metals of this group are precipitated upon acidification of ammonium sulphide extract containing thiosalts of this group of metals. Some sulphur is also liberated from ammonium sulphide.

$$2AsS_4^{-3}+6H^+ = As_2S_5+3H_2S$$
$$2SbS_4^{-3}+6H^+ = Sb_2S_5+3H_2S$$
$$SnS_3^{-2}+2H^+ = SnS_2+H_2S.$$

Sulphides of antimony and tin dissolve in concentrated HCl whereas arsenic sulphide remains undissolved:

$$Sb_2S_5+6HCl = 2SbCl_3+2S+3H_2S$$
$$SnS_2+4HCl = SnCl_4+2H_2S.$$

The addition of iron powder to the filtrate (diluted with water) from HCl treatment causes reduction of $SbCl_3$ and $SnCl_4$ to black Sb and $SnCl_2$ respectively. Tin is identified by the fact that $SnCl_2$ reduces $HgCl_2$ solution to Hg_2Cl_2 (white) and sometimes to metallic mercury (if an excess of $SnCl_2$ be present).

$$2SbCl_3+3Fe = 2Sb+3FeCl_2$$
$$SnCl_4+Fe = SnCl_2+FeCl_2$$
$$SnCl_2+2HgCl_2 = SnCl_4+Hg_2Cl_2 \text{ (white ppt.)}$$
$$SnCl_2+Hg_2Cl_2 = SnCl_4+2Hg \text{ (grey ppt.)}$$

The filtrate (from HCl treatment) containing chlorides of tin and antiomny is made just alkaline with NH_4OH. The addition of excess of oxalic acid to this solution causes the formation of tin oxalato complex ion, in which tin remains in the anion. The behaviour of antimony compound towards oxalic acid is different or at least the antimony oxalato complex is unstable and quite appreciable concentration of cationic antimony ions exists in solution. Hence if H_2S is passed through the solution, only antimony is thrown out of solution as Sb_2S_3, which is identified by its characteristic orange colour.

In one confirmatory test for arsenic, the insoluble residue from HCl treatment is converted into H_3AsO_4 by treatment with nitric acid. The arsenic acid, H_3AsO_4 on being treated with NH_4OH and magnesia mixture is converted into $Mg(NH_4)AsO_4$ and the latter on reaction with $AgNO_3$ gives chocolate-coloured Ag_3AsO_4.

$$3As_2S_5+10HNO_3+4H_2O = 6H_3AsO_4+10NO+15S$$
$$H_3AsO_4+MgCl_2+3NH_4OH = Mg(NH_4)AsO_4+2NH_4Cl+3H_2O$$
$$Mg(NH_4)AsO_4+3AgNO_3 = Ag_3AsO_4+Mg(NO_3)_2+NH_4NO_3$$

In another confirmatory test, the residue is dissolved in $(NH_4)_2CO_3$ solution. Acidification of the resulting solution results in the reprecipitation of As_2S_5.

$$As_2S_5+3(NH_4)_2CO_3 = (NH_4)_3AsS_4+(NH_4)_3AsO_3S+3CO_2$$
$$2(NH_4)_3AsS_4+6HCl = As_2S_5+6NH_4Cl+3H_2S.$$

TABLE 7

Analysis of Group IIIA Metals

Add a few drops of conc. HNO_3 to the solution containing metals of this group or to the filtrate from Group II [after complete removal of H_2S]. Boil for a few minutes. Add about 3-4 gms. of solid NH_4Cl per 20-30 ml. of solution and heat to boiling. Now add NH_4OH dropwise till a slight smell of ammonia persists even on boiling. Boil for a minute and filter.

Residue: May contain $Fe(OH)_3$ brown, $Al(OH)_3$ white gelatinous, $Cr(OH)_3$ greenish and a little $MnO(OH)_2$. Wash the ppt. with hot water and transfer into a beaker. Add a little water and about 1 gm. of Na_2O_2, a little at a time. Boil the mixture till effervescence ceases. Dilute with water and filter.		**Filtrate:** Reject it, if metal or metals of only this group be supplied. Otherwise examine for succeeding groups.
Residue: May contain $Fe(OH)_3$ and often $MnO(OH)_2$. Divide the residue into *two* portions: (*i*) Dissolve one portion in dil HCl by warming and add a few drops of potassium ferrocyanide solution to it. A deep-blue ppt. (prussian blue) confirms *Iron.* (*ii*) Dissolve another portion of the residue in HNO_3(1:1). Add about 1 gm. of Pb_3O_4 or PbO_2. Boil gently for about a minute or two. Dilute and allow the residue to settle. A pink or violet colour of the supernatant liquid confirms *Manganese.*	**Filtrate:** May contain Na_2CrO_4 and $NaAlO_2$. If the filtrate is yellow, divide it into *three* parts (if colourless Cr is absent): (*i*) Acidify one portion with acetic acid and add lead acetate solution—a yellow ppt. of $PbCrO_4$ confirms *Chromium.* (*ii*) Acidify another portion with dil H_2SO_4. Cool under a tap. Add 2 c.c. ether, 2-3 drops of H_2O_2 and shake, a deep-blue etherial layer confirms *Chromium.* (*iii*) Acidity the remaining portion* of the filtrate with dil. HCl (test with litmus). Add NH_4OH till alkaline. Heat to boiling and allow to stand—a white gelatinous ppt. indicates *Al.* Confirm Al by performing cobalt nitrate test with precipitated $Al(OH)_3$.	

*__Alternatively,__ boil the solution with an excess of NH_4Cl—a white gelatinous ppt. confirms *Aluminium.*

Principles underlying the Analysis of Group IIIA Metals

In presence of NH_4Cl, NH_4OH precipitates metals of this group as hydroxides. NH_4Cl reduces the concentration of OH^- ions by common ion effect and buffer action and thus prevents the metals of succeeding groups from being precipitated as hydroxides, which have higher solubility product values than those of the hydroxides of this group of metals. But Mn^{++} ion, if present, may however, be precipitated as higher hydrated oxides, the formation of which is partially due to oxidation of some $Mn(OH)_2$ by air and also partially to oxidation of some Mn^{+2} ions to Mn^{+4} ions during HNO_3 or bromine water treatment meant primarily for oxidation of Fe^{+2} to Fe^{+3} ions.

On boiling the ppt. of the group with NaOH solution and H_2O_2 or simply with Na_2O_2 and water, $Al(OH)_3$ and $Cr(OH)_3$ dissolve forming $NaAlO_2$ and Na_2CrO_4 respectively. In the latter case the solution turns yellow. [The $Fe(OH)_3$ and $MnO(OH)_2$, if present, do not go into solution]. The reactions may be represented by the following equations:

$$Na_2O_2+2H_2O = 2NaOH+H_2O_2$$

$$Al(OH)_3+NaOH = NaAlO_2+2H_2O$$

$$Cr(OH)_3+NaOH = NaCrO_2+2H_2O$$

$$2NaCrO_2+2NaOH+3H_2O_2 = 2Na_2CrO_4+4H_2O.$$

The filtrate obtained on treatment with Na_2O_2 (or, NaOH and H_2O_2), if boiled with NH_4Cl itself or with $HCl+NH_4OH$, $NaAlO_2$ is decomposed and precipitation of $Al(OH)_3$ occurs.

$$NaAlO_2+NH_4Cl+H_2O=Al(OH)_3+NH_3+NaCl.$$

While chromium is tested for in the yellow solution of sodium chromate and these tests involve the conversion of Na_2CrO_4 (*i*) into $PbCrO_4$, insoluble in acetic acid and (*ii*) into perchromic acid H_3CrO_8, which, when shaken with ether, turns the latter blue.

(*i*) $2Na_2CrO_4+2C_2H_4O_2=Na_2Cr_2O_7+2NaC_2H_3O_2+H_2O$

$Na_2Cr_2O_7+2Pb(C_2H_3O_2)_2+H_2O$
$=2PbCrO_4+2NaC_2H_3O_2+2C_2H_4O_2$

(*ii*) $2Na_2CrO_4+H_2SO_4=Na_2Cr_2O_7+Na_2SO_4+H_2O$

$Na_2Cr_2O_7+H_2SO_4+7H_2O_2=2H_3CrO_8+Na_2SO_4+5H_2O.$

The test for iron in the residue containing $Fe(OH)_3$ and $MnO(OH)_2$ (if there be any) involves the treatment of a portion of the residue with dil. HCl followed by addition of $K_4Fe(CN)_6$ solution to the resulting HCl solution, when $Fe_4[Fe(CN)_6]_3$ is produced.

$$FeCl_3+3K_4[Fe(CN)_6]=Fe_4[Fe(CN)_6]_3+12KCl.$$

While the test for manganese in the same residue consists in the conversion of Mn-ppt. into MnO_4^- ion. A portion of the residue obtained after removal of aluminium and chromium from Group IIIA ppt. by boiling with Na_2O_2 and water is boiled with HNO_3 and PbO_2 (or Pb_3O_4), when MnO_4^- ions characterised by its pink colour is produced. The reaction that occurs is represented by the following equation:

$$\begin{aligned}&2Mn(NO_3)_2+5PbO_2+6HNO_3\\&\qquad=5Pb(NO_3)_2+2HMnO_4+2H_2O.\end{aligned}$$

Note that in the usual division of metallic ions into groups, manganese does not come under this group (*i.e.*, Group IIIA). But, in practice, because of some such reasons as have already been stated, some manganese may be precipitated by Group IIIA reagents. Hence provision has been made for detection of manganese in both Group IIIA and IIIB.

TABLE 8

Analysis of Metals of Group IIIB

To the filtrate from Gr. IIIA add a little more NH_4OH (or, to the solution containing metals of this group add about 3-4 gms. of solid NH_4Cl as usual and heat to boiling. Now add NH_4OH to render the solution ammoniacal). Warm and then pass H_2S. Filter.

<table>
<tr>
<td colspan="3">Residue:
May contain ZnS (white), MnS (flesh coloured), NiS and CoS (both black). Wash the residue with 1% NH_4Cl solution containing a little ammonium sulphide. Transfer the residue into a beaker and add about 25 c.c. of very dil. HCl (1 : 10); stir with a glass rod for about 5 to 6 minutes and filter.</td>
<td rowspan="3">Filtrate:
Examine it for metals of succeeding groups. But if metal or metals of this group only be supplied, neglect the filtrate.</td>
</tr>
<tr>
<td rowspan="2">Residue:
If black, either NiS or CoS or both are present. In such a case perform the following tests:
(<i>i</i>) Perform Borax Bead Test by fusing a little of the residue on borax bead. Note the colour of the bead. Sapphire blue bead confirms <i>Cobalt</i>. But a reddish-brown bead shows <i>Nickel</i>.
(<i>ii</i>) Dissolve a little of the residue by heating with a minimum volume of conc. HCl together with a few crystals of $KClO_3$. Evaporate nearly to dryness. Cool and</td>
<td colspan="2">Filtrate:
May contain $MnCl_2$ and $ZnCl_2$. Boil off H_2S completely (test with lead acetate paper). Cool and add an excess of NaOH solution. Stir with a glass rod. Warm a a little, cool and filter.</td>
</tr>
<tr>
<td>Residue:
White; $Mn(OH)_2$ which may turn brown due to atmospheric oxidation.</td>
<td>Filtrate:
May contain Na_2ZnO_2. Divide the filtrate into <i>two</i> parts:
(<i>i</i>) Through one part of the filtrate</td>
</tr>
</table>

dilute with water. Divide the solution into *two* parts:		(*i*) Dissolve a little of the residue in 1 : 1 HNO_3. Add about 1 gm. of PbO_2 or Pb_3O_4. Boil for a minute. Dilute with water and let stand. Pink or violet colour of the supernatant liquid confirms *Manganese*. (*ii*) Perform Borax Bead Test with a little of the residue and note the colour of the bead—amethyst bead confirms *Manganese*. [Student may confirm Mn by 'Oxidising Fusion Test' also. *See* page 20.].	pass H_2S—a white ppt. of ZnS shows *Zinc*. (*ii*) Acidify the second portion with acetic acid. Add a solution of $K_4Fe(CN)_6$—appearance of white ppt. confirms *Zinc*.
To one part add NH_4OH till alkaline. Add a few drops of dimethyl glyoxime—a red ppt. confirms *Nickel*.	(*i*) To a little of the second portion add acetic acid and a little KNO_2.* Let it stand with occasional scratching and shaking. A yellow ppt. of Potassium cobaltinitrite shows *Cobalt*. (*ii*) To a portion of the solution add about 2-3 gms. of solid NH_4CNS, 2 cc. amyl alcohol and shake. Blue colour of alcoholic layer shows *Cobalt*.		

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*KNO_2 is very rare in the laboratory. It may be replaced by excess of solid $NaNO_2$+a small crystal of KCl.

Principles of Analysis of Metals of Group IIIB

Addition of ammonium sulphide (*i.e.*, NH_4OH+H_2S) causes precipitation of sulphides of these metals.

Of these sulphides MnS and ZnS are soluble in very dil. HCl (1 : 10), while NiS and CoS are practically insoluble.

$$MnS+2HCl = MnCl_2+H_2S$$
$$ZnS+2HCl = ZnCl_2+H_2S.$$

The solution obtained on treatment of the sulphide with very dil. HCl may contain Zn^{++} ions and Mn^{++} ions. If this solution be treated with excess of NaOH solution, the hydroxides are first precipitated. But $Zn(OH)_2$, however, goes into solution with the excess of NaOH solution forming ZnO_2^{-2} ion whilst hydroxide of manganese remains unaffected and is separated by filtration.

$$ZnCl_2+4NaOH=Na_2ZnO_2+2NaCl+2H_2O$$
$$MnCl_2+2NaOH=Mn(OH)_2+2NaCl.$$

The precipitated hydroxide of manganese is then oxidised by boiling with HNO_3 and PbO_2 (or Pb_3O_4) to MnO_4^- ion, which is characterised by its pink colour.

$$2Mn(NO_3)_2+5PbO_2+6HNO_3$$
$$=5Pb(NO_3)_2+2HMnO_4+2H_2O.$$

H_2S precipitates ZnS (white) from the filtrate containing ZnO_2^{-2} ions.

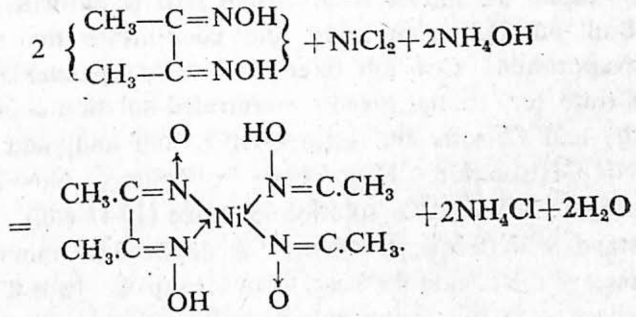
$$Na_2ZnO_2+H_2S=ZnS+2NaOH.$$

Zinc is also characterised by a white ppt. of $K_2Zn_3[Fe(CN)_6]_2$ obtained in the dil. acid medium on addition of $K_4[Fe(CN)_6]$.

The residue left over after the treatment of sulphides with very dil. HCl (1 : 10) may contain NiS and CoS. This is brought into solution either by treating with *aqua regia* or by treating with conc. HCl together with a few crystals of $KClO_3$ in the usual way.

$$3NiS+2HNO_3+6HCl=3NiCl_2+2NO+3S+4H_2O$$
$$3CoS+2HNO_3+6HCl=3CoCl_2+2NO+3S+4H_2O;$$

To a portion of the solution thus obtained NH_4OH is added till alkaline and then a few drops of dimethyl glyoxime reagent —a red ppt. of Nickel dimethyl glyoxime confirms Ni.



Cobalt is detected by carrying out the test, which is based upon the following equation:

$$Co^{++}+7NO_2^{-}+3K^{+}+2H^{+}\rightarrow K_3[Co(NO_2)_6]+NO+H_2O.$$

Cobalt can also be confirmed by carrying out the Borax Bead Test with the residue (a mixture of NiS and CoS), which is left behind after the treatment of the precipitated sulphides of this group with very dilute HCl. In NH_4CNS test for cobalt, ammonium cobalto thiocyanate $(NH_4)_2[Co(CNS)_4]$, which is blue in colour is formed. This compound being stable and soluble in amyl alcohol imparts a blue colour to alcoholic layer. Fe^{+++}, if present, interferes with this test as a red coloured complex $[Fe(CNS)_6]^{-3}$ is formed.

TABLE 9

Analysis of Group IV Metals

Make the filtrate from Group IIIB acidic with acetic acid. Boil off H_2S completely and concentrate the solution by evaporation. Cool and filter, if any solid separates out. To this filtrate [or, to the given concentrated solution containing Ba-, Sr- and Ca-salts add solid NH_4Cl, boil and] add 2-3 c.c. of NH_4OH solution. Heat nearly to boiling. Now add freshly prepared $(NH_4)_2CO_3$ solution in excess (10-15 c.c.). Allow it to stand with frequent stirring for about 5-10 minutes. Filter, reserve the filtrate for analysis of Group V. [But if the radicals given be of this group only discard the filtrate.] Examine the precipitate for metals of Group IV in the following way:

<table>
<tr><td colspan="3">Residue: May contain carbonates of Ba, Sr and calcium. Wash the residue with hot water. Dissolve the precipitate by pouring down the minimum volume of hot, dilute acetic acid on the filter paper. Collect the solution in a beaker by placing it under the funnel. Heat the solution to boiling. Test a little of this solution for barium by adding a few drops of K_2CrO_4 solution to it. If <i>no ppt.</i>, Ba is absent; don't add K_2CrO_4 to the whole of the solution but proceed forthwith for testing Ca and Sr. If a <i>yellow ppt.</i> appears, Ba is present. Treat the main bulk of the hot solution with K_2CrO_4 solution in slight excess. Filter.</td></tr>
<tr><td>Residue: Yellow $BaCrO_4$. Wash with water and perform flame test with a little of this washed residue. Apple green flame shows <i>Barium.</i></td><td colspan="2">Filtrate*: May contain Sr and Ca salts. Render it alkaline by adding NH_4OH. Add a saturated solution of ammonium sulphate. Heat to boil and allow it to stand at least for five minutes. A white ppt. of $SrSO_4$ indicates Sr^{+2}. [If K_2CrO_4 is used for separation of Ba^{+2}, this white colour becomes apparent only after washing the ppt. with water.] Filter.</td></tr>
<tr><td>Dissolve a little of the residue in dil. HCl and add a few drops of dil. H_2SO_4—a heavy white ppt. confirming <i>Barium.</i> [This ppt. may appear yellow but becomes white, if washed well with water.]</td><td>Residue: Reduce the precipitated $SrSO_4$ by heating a little of it on the tip of a wire in the luminous flame and then perform with the reduced product the flame test in the usual way. A steady crimson flame confirms <i>Strontium.</i></td><td>Filtrate: May contain Ca-salt.
Add NH_4OH and ammonium oxalate solution—a white crystalline precipitate, insoluble in acetic acid confirming <i>Calcium.</i>
Perform flame test for <i>Calcium.</i></td></tr>
</table>

*An alternative but perhaps a better method for detecting Sr^{+2} is to treat a portion of it with a saturated solution of $CaSO_4$ and allow to stand, when a white ppt. of $SrSO_4$ is obtained. Confirm Sr^{+2} by performing flame test with this ppt. as usual.

Principles of Analysis of Metals of Group IV

Advantage is taken of the following facts:

The addition of NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ causes precipitation of sparingly soluble $CaCO_3$, $SrCO_3$ and $BaCO_3$. The presence of ammonium ion lowers the concentration of CO_3'' ions and OH^- ions so much so that magnesium, if present in the solution, is not precipitated. Too large excess of NH_4Cl hinders even the precipitation of carbonates of Ba, Sr and Ca. Hence excess of NH_4Cl, if present, is to be removed by crystallisation from the filtrate of Group IIIB before trying to precipitate out metals of Group IV. Moreover, the solution should not be boiled with $(NH_4)_2CO_3$, as boiling causes volatilisation (*cf.* page 45) of $(NH_4)_2CO_3$ and thus lowers the concentration of CO_3'' ions.

Carbonates of Ba, Sr and Ca on being treated with acetic acid pass into solution with the formation of acetates, carbon dioxide being evolved. When this acetic acid solution is treated with a solution of K_2CrO_4, only Ba is precipitated as $BaCrO_4$. But $SrCrO_4$ and $CaCrO_4$ being soluble in the medium are held in solution. Ba^{++} ions are thus separated from Sr^{++} and Ca^{++} ions.

$$BaCO_3+2CH_3COOH=(CH_3COO)_2Ba+CO_2+H_2O$$

$$(CH_3COO)_2Ba+K_2CrO_4=BaCrO_4+2CH_3COOK.$$

$BaCrO_4$ dissolves in HCl forming $BaCl_2$, which, on treatment with dil. H_2SO_4, gives a heavy white ppt. of $BaSO_4$.

The filtrate obtained after the addition of K_2CrO_4 contains Sr^{++} ions and Ca^{++} ions. This filtrate is made ammoniacal by addition of NH_4OH. Concentrated solution of $(NH_4)_2SO_4$ precipitates out $SrSO_4$ from this ammoniacal solution. But $CaSO_4$ dissolves in hot conc. $(NH_4)_2SO_4$ solution forming the soluble $(NH_4)_2Ca(SO_4)_2$. Some $CaSO_4$ may be co-precipitated with $SrSO_4$, if the concentration of Ca^{++} ions be very high. [In an alterative method as described in foot-note under Table 9 the detection of Sr^{+2} involves the precipitation of $SrSO_4$ by a saturated solution of $CaSO_4$, the use of which is preferable to that of other soluble sulphates or dil. H_2SO_4]. The filtrate, obtained after the separation of $SrSO_4$, contains Ca^{++} ions. The filtrate, if treated with NH_4OH and $(NH_4)_2C_2O_4$ yields a ppt. of CaC_2O_4 because CaC_2O_4 is less soluble than $CaSO_4$.

TABLE 10

Analysis of Group V

Mg^{++}-, K^{+}-, Na^{+}- & NH^{+}_{4} -ions

To the filtrate from Group IV add 2 c.c. each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ solution. Heat to boiling and allow it to stand at least for 5 minutes. Filter, if any ppt.[1] comes down. Divide this filtrate (or, concentrated solution containing metals of this group) into two unequal parts.

<table>
<tr><td rowspan="2">To the smaller portion add NH_4OH and then Na_2HPO_4 solution in excess. Shake well and scratch the sides of the testtube with a glass rod and let stand. A white crystalline ppt.[2] shows <i>Magnesium</i>.</td><td colspan="2">Evaporate the larger portion to dryness and heat the residue below dull redness till the evolution of white fumes of ammonium salt ceases. Again evaporate it to dryness with a little conc. HNO_3 and heat gently to expel the ammonium salt, if any.
If no residue Na, K are absent. Further analysis is unnecessary. Perform the usual test for ammonia[5] with the original sample or with its aqueous extract.
If any residue, cool it, take up with about 3 c.c. of water and filter. Divide the filtrate into <i>two</i> parts.</td></tr>
<tr><td>To one part add a little acetic acid and freshly prepared sodium cobalti-nitrite solution. Shake and allow to stand for a few minutes. A yellow ppt.[3] of $K_2Na[Co(NO_2)_6]$ shows <i>Potassium</i>.
Confirm potassium by performing flame test with the original solid (or, better with residue obtained by evaporating the aqueous extract of the sample).</td><td>To the other part[4] add a little potassium antimonate solution. Rub the inside of the test-tube with a glass rod; a crystalline white ppt. of NaH_2SbO_4, which sticks to the wall of the test-tube like sandy particles shows <i>Sodium</i>.
Confirm sodium by flame test (<i>see</i> potassium).</td></tr>
</table>

Since ammonium[5] compounds are added at various stages during the course of analysis, don't test for it in the filtrate from Group IV. Perform the following tests for NH_4^+:

Heat the original substance with NaOH solution; the gas evolved has a pungent smell, turns red litmus blue and filter paper moistened with mercurous nitrate solution black—ammonium compounds. *See* pages 21,73.

Notes on Table 10

1. The alkaline earth metals that have escaped precipitation in Group IV are precipitated here. So, in case any precipitation occurs here, examine the ppt. for metals of Group IV.

2. Aluminium, if not precipitated completely in its proper place, may be precipitated here as $AlPO_4$. Note that in the case of aluminium a flocculant precipitate but in the case of Mg a crystalline ppt. of $MgNH_4PO_4$ comes down. Treat the ppt. with acetic acid. If it dissolves—Mg, since $MgNH_4PO_4$ is soluble in acetic acid where as $AlPO_4$ is not.

N.B. It often happens if metals of preceding groups escape precipitation in their proper places, they are precipitated on addition of Na_2HPO_4 and students consequently report for Mg even when no Mg is present.

3. This test for potassium does not hold good in presence of ammonium salts, since ammonium salts also give a similar coloured ppt. with the reagent. So perform this test for potassium with the solution from which ammonium salts have been completely removed. Prepare sodium cobaltinitrite solution by mixing an equal volume of cobalt nitrate and a strong solution of sodium nitrite (20 gms. in 30 c.c. water). Add a little excess of acetic acid to the mixed solution. Use the solution thus prepared.

4. This solution must not be too dilute. Of the various reagents proposed from time to time for testing Na, zinc uranyl acetate or magnesium uranyl acetate is satisfactory. Note that the flame colour is characteristic and hence is confirmatory test for both Na and K.

5. An extremely sensitive test for ammonia is with Nessler's reagent. To a little of the aqueous extract of the original sample add Nessler's reagent; a brown coloration or an orange-red ppt. depending upon the amount of ammonia is obtained.

N.B. In this experiment all metal except those of alkalis must be absent. Hence it is preferable to carry out this test with the gas obtained on heating the sample with alkali.

Preparation of Nessler's reagent:

It is an alkaline solution of potassium mercuri-iodide. Prepare Nessler's reagent by adding KI solution to a solution of mercuric chloride when a red ppt. is formed and then dissolving this ppt. of HgI_2 in *just excess* of potassium iodide solution. Now make the solution alkaline by adding KOH.

Chemistry of the Analysis of Group V

No satisfactory systematic scheme being available for the qualitative analysis of Group V, the radicals are looked for by independent tests. It utilises the following facts:

1. To a solution of magnesium compounds containing NH_4Cl and NH_4OH addition of Na_2HPO_4 causes a ppt. of white crystalline magnesium ammonium phosphate.

$$MgCl_2+NH_4OH+Na_2HPO_4=Mg(NH_4)PO_4+2NaCl+H_2O.$$

The precipitation is accelerated by concentrating the solution before addition of the reagent and by vigorous shaking and scratching the inner wall of the test-tube. Since alkaline earth metals also give ppt. with Na_2HPO_4, they are first of all removed (if there be any) by adding $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$.

2. Addition of sodium cobaltinitrite to a solution containing K^+ ions gives a yellow ppt. of potassium-sodio-cobaltinitrite $K_2Na[Co(NO_2)_6]$.

$$Na_3[CO(NO_2)_6]+2KCl=K_2Na[Co(NO_2)_6]+2NaCl.$$

This precipitation reaction is shown by NH_4^+ ions also. Hence this test for K^+ ion should be performed in absence of NH_4^+ ion. To detect K^+ ion in presence of NH_4^+ ion, the latter is expelled first (the procedure is shown in the table) and then the test is performed.

3. Weakly alkaline or neutral solution of sodium compounds when treated with a solution of potassium antimonate gives a white crystalline ppt. of sodium antimonate.

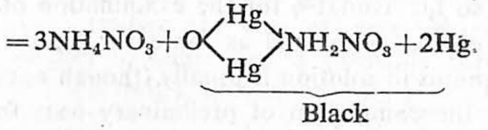
$$KH_2SbO_4+NaCl=NaH_2SbO_4+KCl.$$

The precipitation is facilitated by scratching the inside of the test-tube.

4. Ammonium salts, when heated with NaOH solution, ammonia is evolved.

$$NH_4Cl+NaOH=NH_3+NaCl+H_2O.$$

The evolved ammonia turns mercurous nitrate paper black, $2Hg_2(NO_3)_2+4NH_3+H_2O$



$$=3NH_4NO_3+\underbrace{O\left\langle\begin{matrix}Hg\\ \\ Hg\end{matrix}\right\rangle NH_2NO_3}_{\text{Black}}+2Hg.$$

Moreover, mercuric chloride when treated with excess of KI, a complex compound, potassium mercuri-iodide is produced in solution. An alkaline solution of this reagent gives brown coloration or an orange-red ppt. with ammonia.

$$HgCl_2+2KI=HgI_2+2KCl$$
$$HgI_2+2KI=K_2[HgI_4]$$
$$2K_2[HgI_4]+3KOH+NH_3=\underbrace{IHg\text{-}O\text{-}HgNH_2}+7KI+2H_2O.$$

The formula of the ppt., which is known as iodide of Milon's base is shown above within the second bracket.

CHAPTER V

Examination of Anions in Solution

The methods so far available for the examination of anions in solutions are not so systematic as those for basic radicals. Examination of anions in solution is usually (though not always) carried out after the completion of preliminary tests for basic and acid radicals, the special tests for some acid and basic radicals and the wet analysis of the basic radicals. The knowledge gathered from the tests so performed and the behaviour of the substance towards different solvents give some indications as to the presence and absence of many acidic radicals. Suppose the substance is soluble in water and the basic radicals of the Group IV (*i.e.*, barium group) are present, then sulphuric acid, carbonic acid and phosphoric acid are not present. Similarly, chlorides, bromides and iodides are definitely absent should the sample be soluble in water and silver have been found. The students, therefore, should carry out the test for anions, in a judicious and intelligent way.

Preparation of Solution for Examination of Anions

In order to avoid side reactions, prepare a solution which will contain all anions free, as far as possible from heavy metals. This is done in the following way:

Take a little of the substance in a beaker. Add about 5 times its weight of Na_2CO_3 and about 20 c.c. distilled water. Boil at least for 15 minutes making up the loss of water that takes place during evaporation by adding distilled water; boil, cool and filter.

[If the substance is soluble in water and contains no heavy metals, the aqueous solution obtained by boiling the substance with water *may be examined* for anions. In fact the examination of aqueous extract for the detection of anions may sometimes prove advantageous. If the substance be only partly soluble in water, as it often happens in the case of mixture, the following method of preparing solution may be adopted:

Boil the substance first with water and then treat the warm aqueous extract thus obtained with a concentrated solution of Na_2CO_3 to precipitate out heavy metals, if there by any.

Filter. Take the residue (obtained from treatment of the substance with water), fuse it with solid Na_2CO_3 and extract with water. Analyse the two extracts separately. This may help a student in suggesting a probable composition of the mixture with a certain degree of accuracy.].

Tests for Anions

Use a portion of the solution thus prepared for performing the tests for anions and reserve the remaining portion for the separation of mixture of acids, if necessary.

Experiments	Observations	Inferences
1. To a little of the prepared solution add a few drops of freshly prepared sodium nitroprusside solution.	A transient pink or violet colour.	Sulphide[1]
2. Acidify a little of the prepared solution with dil, HCl. Boil off CO_2 and add $BaCl_2$ solution.	(*a*) Sometimes a gelatinous ppt. appears on acidification, particularly on boiling.	Silicate
	(*b*) A heavy white ppt. insoluble in excess of dil. HCl.	Sulphate
3. Acidify a little of the prepared solution with dil. HNO_3. Boil off CO_2 and add $AgNO_3$ solution.	(*a*) A white ppt. insoluble in dil. HNO_3 but soluble in ammonia.	Chloride
	(*b*) A pale-yellow ppt., insoluble in dil. HNO_3, soluble in excess of *strong* ammonia.	Bromide [4]
	(*c*) A yellow ppt. insoluble in dil. HNO_3 and does not dissolve in strong ammonia.	Iodide
3. (*i*) If any positive evidence be obtained in in expt. 3, evaporate a portion of Na_2CO_3 extract and perform *chromyl chloride* test with the residue (*see* page 84).	Yellow ppt.	Chloride

Experiments	Observations	Inferences
4. Acidify 1 c.c. of the prepared solution with dil. H_2SO_4 and wait till the effervescence ceases; add 1 c.c. of a freshly prepared saturated solution of ferrous sulphate. Now add 1-2 c.c. conc. H_2SO_4 cautiously down the side of the test-tube without disturbing the liquid.	A brown ring is formed at the junction of the two liquid layers.	Nitrate[2] and/or nitrite.
5. Acidify a little of the prepared solution with dilute acetic acid and divide the solution into *two* parts:		
(*i*) (*a*) To one part add starch-KI solution.	A deep-blue coloration.	Nitrite and/or other oxidising agents.
(*b*) If no deep-blue colour develops in 5(*i*)(*a*) add a piece of zinc.	A deep-blue colour develops.	Nitrate
(*ii*) Boil off CO_2 from the second portion and add lead acetate solution.	Yellow precipitate	Chromate[3] and/or iodide.
6. Acidify a little of the prepared solution with dil. HCl. Boil off CO_2; make it alkaline with NH_4OH; then add magnesia mixture.	A white ppt.	Arsenate and/or phosphate.) } 5
7. Filter the ppt. obtained in Experiment (6), acidify the filtrate with dil. HCl; warm and pass sulphuretted hydrogen.	A yellow ppt.	Arsenite
8. Acidify a little of the prepared solution with dil. HNO_3, boil off CO_2. Now add NH_4OH to make the solution just alkaline; boil off excess of ammonia and divide the neutral solution into two parts.		

If the substance be insoluble in water, appearance of an orange or yellow ppt. on neutralisation of Na_2CO_3 extract with acid indicates the presence of sulphide of Sb or As.

Experiments	Observations	Inferences
(*i*) To one part add an excess of $AgNO_3$ solution.	(*a*) A yellow ppt.	Phosphate and/or Iodide.
	(*b*) A red-brown ppt.	Arsenate and/or arsenite.
	(*c*) A chocolate red ppt.	Chromate
	(*d*) Yellowish-white or white ppt. insoluble in HNO_3.	Halides^4
(*ii*) To the other part, add a freshly prepared dilute solution of $FeCl_3$ drop by drop.	(*a*) Yellowish-white ppt. soluble in dil. mineral acids but insoluble in dil acetic acid.	Phosphate^5
	(*b*) Blood-red coloration bleached by $HgCl_2$ but not by HCl.	Thiocyanate

N.B. 1.4. Acid radicals in some sulphides and halides cannot be detected by the preliminary tests and also by the tests described above. So if a student suspects the presence of halides and/or sulphide (in fact, after the completion of the wet analysis of the base attempt should always be made to guess the presence or absence of particular acid or acids from a knowledge of the solubility of the substance supplied) he should perform the special tests for sulphides and halides as indicated earlier under "some special tests for detection of acid radicals".

2. The brown ring is due to the formation of a compound, which is formulated as $[Fe(NO)]SO_4$.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO = [Fe(NO)]SO_4.$$

Bromide, Iodide must be absent. Note that this test is not reliable in presence of sulphites, thiosulphates, chromates, etc.

3. Perform the experiment for chromate, if the perpared solution is coloured yellow.

5. Test for phosphate should also be carried out in the filtrate from Group II, if its presence is suspected by the preliminary test.

Examination of acid mixture for detection of Constituent acids

When the sample supplied contains more than one acid radical, the identification of the acid radicals often becomes a bit difficult, one masking the presence of another. If the presence of any acid radical be indicated or suspected at any stage during the course of analysis the suspected acid should be confirmed by at least one distinctive confirmatory test. Moreover, the substance must be examined for other acids (or acid), which are similar to the suspected acid and which are likely to interfere with the identification of the suspected acid.

1. Mixture of Carbonate and Sulphite:

Experiment:

Mix the solid with a little $K_2Cr_2O_7$ and take it in a test-tube; add dil. H_2SO_4, warm, if necessary. (*a*) Pass the evolved gas through clear lime water and (*b*) observe the colour of the mixture in the test-tube to which H_2SO_4 has been added.

Observations	Inferences
(*a*) Lime water turns milky.	(*a*) Carbonate
(*b*) The solution in the test-tube becomes green.	(*b*) May be Sulphite

N.B. Note that the presence of these acids are indicated in the preliminary test, which consists in treating the substance with dil. acid and passing the evolved gas through lime water, when the latter turns milky.

If the solution in the test-tube becomes green, onfirm sulphite by the method given for analysis of mixture of sulphur acids (*see* page 82).

2. Mixture of Nitrate and Nitrite

Experiment (*i*):

Acidify a little of the prepared solution with dil. H_2SO_4 add KI and starch solution.

Observation	Inference
The solution turns deep-blue	**Nitrite**

Experiment (*ii*):

Boil another portion of the solution with ammonium chloride or with urea and dil. H_2SO_4 till the effervescence or evolution of gas ceases. Now apply *either* (a) the ring test for nitrate with the residual solution *or*, (*b*) add KI and starch solution and a piece of zinc to the residual solution and then acidify with dil. H_2SO_4.

Observations	Inferences
(*a*) A brown ring is formed ... (*b*) Deep-blue colour is developed in solution...	(*a*) Nitrate (*b*) Nitrate

N.B. Nitrite can be identified even in presence of a nitrate. But nitrite interferes with the test for a nitrate, the identification of which, therefore, necessitates the previous removal of nitrite. To test for nitrate in the mixture, nitrite is first decomposed either by boiling the substance with ammonium chloride or with urea and dil. H_2SO_4. Reactions that occur while decompsing a nitrite are:

$$NaNO_2+NH_4Cl=NaCl+N_2+2H_2O$$
$$2HNO_2+CO(NH_2)_2=CO_2+2N_2+3H_2O.$$

(*i*) Note that small amounts of nitrate are always formed while destroying nitrites by the above methods

(*ii*) The presence of these acids are indicated while warming the substance with conc. H_2SO_4—a brown fume being evolved. These are also indicated by ring test. [*See also* the experiment (*a*) and connected notes described for the analysis of Acid mixture no. 7.].

3. Mixture of Arsenite, Arsenate and Phosphate

To the prepared solution add dil. HCl till faintly acid, boil off CO_2. Now make the solution alkaline with NH_4OH and add an excess of magnesia mixture; rub the walls of the vessel and let it stand for 5-10 minutes. Filter.

<table>
<tr><td rowspan="2">**Filtrate:** Acidify with dil. HCl, heat to boiling and pass in H_2S. A *yellow ppt.* of arsenious sulphide confirms *Arsenite.*</td><td colspan="2">**Residue:** White ppt., wash with water. Dissolve the ppt. in dil. HCl. Add sulphurous acid. Boil off excess of sulphur dioxide; pass in H_2S. If yellow ppt. appears, pass in more H_2S till precipitation is complete. Filter.</td></tr>
<tr><td>**Residue:** *Yellow ppt.* of arsenious sulphide indicates *Arsenate.*</td><td>**Filtrate:** Boil off H_2S. Add a little conc. HNO_3, now add a little of this filtrate to an excess of ammonium molybdate containing 2-3 c.c. conc. HNO_3. Shake and finally warm. A canary *yellow ppt.* confirms *Phosphate.*</td></tr>
</table>

4. Mixture of Sulphur* acids

Shake up the prepared solution[1] with an excess[2] of $PbCO_3$ suspension in water and filter.

<table>
<tr><td rowspan="3">**Residue:** Black, a mixture of $PbCO_3$ and PbS. The *black colour is* due to PbS. which indicates *Sulphide.*</td><td colspan="3">**Filtrate:** Add $BaCl_2$ solution in excess[2] and filter.</td></tr>
<tr><td colspan="2">**Residue:** White ppt. of $BaSO_4$, $BaSO_3$ and $BaCO_3$. Wash, treat the ppt. with dil. HCl and filter.</td><td rowspan="2">**Filtrate:** Contains BaS_2O_3. Acidify with dil. HCl and boil—*smell* of SO_2 (tested by $K_2Cr_2O_7$ paper) and *precipitation* of sulphur indicates *Thiosulphate.*</td></tr>
<tr><td>**Residue:** *White ppt.* of $BaSO_4$ indicates *Sulphate.*</td><td>**Fitrate:** Contains sulphurous acid. Add bromine water, decolourisation of bromine water and a *white ppt.* of $BaSO_4$ indicates *sulphite.*</td></tr>
</table>

N.B. 1. The prepared solution must not be acidified.

2. Excess of reagent is to ensure complete precipitation.

In place of $PbCO_3$ and $BaCl_2$ use $CdCO_3$ and $Sr(NO_3)_2$ respectively, if available. If $CdCO_3$ is used, a *yellow ppt.* is obtained instead of a black one in case of a sulphide.

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*The presence of sulphur acids is indicated by nitroprusside test performed with the residue of charcoal reduction test.

5. Mixture of Chromate and Sulphate

To test for above acids perform the following experiments:

Experiment (i):

To a little of the prepared solution add dil. H_2SO_4 till acid. Cool under a tap; add a little ether (about 0·5 c.c.) and a drop or two of 3% hydrogen peroxide and shake.

Observation	Inference
The ethereal solution is coloured *blue*, which gradually turns green.	Chromate

Experiment (ii):

Acidify a little of the prepared solution with dil. HCl, boil off CO_2 and add $BaCl_2$ solution. Filter and wash the residue with water till free from yellow colour.

Observation	Inference
A white residue is left behind.	Sulphate

N.B. Note that the individual tests for the constituent acids of the mixture have already been described. Moreover, the above combinations present no special difficulty in their detection. Hence students following the systematic course of analysis must have identified these acids, if present, by performing independent expts., and may intelligently avoid here the mere repetition of the experiment.

6. Mixture of Chloride, Bromide and Iodide

First method:

(*a*) Acidify a little of the prepared solution with dil. H_2SO_4 or dil. HCl, add 1-2 c.c. of carbon tetrachloride (or carbon disulphide). Now add strong chlorine water drop by drop and shake after each addition. The carbon tetrachloride (or, carbon disulphide) layer turns *violet*—this indicates **iodide.** Continue addition of chlorine water. Violet colour disappears and a *reddish* colour appears indicating the presence of **bromide.** If iodide alone be present the carbon tetrachloride (or carbon disulphide) layer becomes *colourless* after the disappearance of violet colour.

N.B.—Excess chlorine destroys colour even that due to bromine.

(*b*) Now confirm chloride by ***any one*** of the following methods:

(*i*) Acidify a little of the prepared solution with dil. HNO_3, boil off CO_2, add an excess of $AgNO_3$ solution. Filter.

<table>
<tr>
<td rowspan="2">Filtrate:
Reject it.</td>
<td colspan="2">Residue:
Wash with water till the washings are free from Ag^+ ions; test the washing with dilute KI (or K_2CrO_4) solution. If no yellow (or red) ppt., Ag^+ ions have been completely removed. (if a yellow or red ppt., repeat the process of washing). Shake the ppt. with 4N $(NH_4)_2CO_3$ solution and filter.</td>
</tr>
<tr>
<td>Filtrate:
Add a few drops of KBr solution, a <i>yellowish-white</i> ppt. indicates <i>Chloride</i>. Or, acidify the filtrate with dil. HNO_3, a <i>curdy-white</i> ppt. indicates <i>Chloride</i>.</td>
<td>Residue:
Reject it.</td>
</tr>
</table>

(*ii*) *Chromyl chloride test*: Mix the solid sample with powdered $K_2Cr_2O_7$ in the ratio of 1 : 2 by weight and take it in a hard glass test-tube. Now add almost an equal bulk of conc. H_2SO_4 to it and warm the test-tube gently. Pass the evolved deep-red gas into caustic soda solution taken in another test-tube. The NaOH solution turns yellow due to formation of alkali chromate. Acidify the solution with acetic acid and add $BaCl_2$ solution—a yellow ppt. indicates chromate proving thereby the presence of **chloride in the sample.**

N.B. The experiment 6*b* (*ii*) for detection of chloride cannot be carried out in presence of fluoride, which yields volatile CrO_2F_2. Moreover, chlorides of Hg, Ag do not respond to this test.

Note that it is risky to carry out the experiment in presence of chlorate, which produces explosive chlorine dioxide.

Reaction occuring in the expt.:

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH = Na_2CrO_4 + 2H_2O + 2NaCl.$$

Second method:

Acidify a portion of the prepared solution with acetic acid, boil off CO_2. Add $CuSO_4$ solution in excess. Filter.

Residue:	**Filtrate:**	
Brown in colour becomes almost *white* on addition of a little thiosulphate solution. *Iodide.*	Boil off iodine and make it faintly alkaline by addition of NaOH. Filter.	
	Residue: Pale-blue ppt. of copper hydroxide. Reject it.	**Filtrate:** Acidify a little of the filtrate with acetic acid, add 1 c.c. of CCl_4 or CS_2. Now add strong chlorine water drop-wise and shake, when CCl_4 (or CS_2) layer turns *brown* indicating thereby the presence of *Bromide.* To confirm chloride perform the tests as under 6(*b*) page 84.

N.B. This method is advantageous for detection of bromide in presence of excess of iodide.

7. Mixture of Nitrate, Bromide and Iodide

(*a*) To a little of the prepared solution add a little caustic soda solution, aluminium powder or zinc dust and warm gently—in case **nitrate** being present evolution of ammonia (detected by its smell) occurs.

(*b*) Perform the experiment as under *Mixture no.* 6 (page 83) with another portion of the prepared solution for detection of **bromide and Iodide.**

N.B. Decompose the ammonium salts, if there by any (while examining an aqueous solution) by boiling with NaOH solution before performing the test for nitrate.

Note that nitrite also responds to this test (*i.e.*, gives off smell of ammonia). Don't perform here the ring test for nitrate, as the liberated halogens (*i.e.*, from bromide and iodide) interfere with this test. Ring test may, however, be performed after the removal of bromide and iodide by treating the solution with nitrate-free **silver sulphate** solution.

8. Mixture of Chromate and Iodide

To a little of the prepared solution add $AgNO_3$ solution till precipitation is complete. Now acidify with dil. HNO_3; warm and filter.

Residue:	Filtrate:
Yellow ppt. indicates *Iodide.*	Neutralise the solution by adding NaOH solution drop-wise–*red ppt.* indicates *Chromate.*

9. Mixture of Nitrite and Iodide

Acidify a little of the prepared solution with dil. H_2SO_4 and add starch solution, the solution turns *deep-blue*, if both **nitrite** and **iodide** be present.

N.B. Note that iodide in presence of an oxidising agent (*e.g.*, nitrite, chromate, etc.) responds to this test. This test is, therefore, not very conclusive, so far as nitrite is concerned. Perform other tests for nitrite. The following test may also be tried: Dissolve a little aniline taken in a test-tube in dil. HCl. Cool under tap. Now add to it the dil. solution of the sample (supposed to contain nitrite) under examination in portions cool again and add a little of this (diazotised) solution to an *excess* of alkaline solution of β-naphthol, an immediate scarlet-red ppt. or coloration indicates the presence of **nitrite.**

10. Mixture of Boric acid and Borate

(*a*) Perform the test for free boric acid in the usual way (*see* page 28). The *green-edged* flame indicates free **boric acid.**

(*b*) Shake well a portion of the substance (original solid) with alcohol. Filter. Perform the test for **borate** (*see* page 29) with the residue. The *green-edged* flame here indicates the presence of **Borate.**

CHAPTER VI

TREATMENT OF INSOLUBLE RESIDUE (OR SAMPLE)

The residue left over after the treatment of the substance with water, acids and *aqua regia* (or, conc. $HCl+KClO_3$) in succession for bringing the substance in solution is described as **insoluble.** Below is given the list of insoluble substances that are encountered in inorganic qualitative analysis:

(*i*) **White**—$PbCl_2$,* $PbSO_4$, $BaSO_4$, $SrSO_4$, $CaSO_4$ †; strongly ignited oxides Al_2O_3, SnO_2, Sb_2O_4 ‡; CaF_2 (native), AgCl §, SiO_2 and various silicates.

(*ii*) **Yellow**—AgBr § (pale-yellow), AgI § (yellow);

(*iii*) **Brown**—Fused $PbCrO_4$;

(*iv*) **Dark-grey**—$FeCr_2O_4$ (Chrome iron ore);

(*v*) **Green**—Cr_2O_3 (ignited);

(*vi*) **Dark-red**—Fe_2O_3‡ (ignited);

(*vii*) **Bronze**—SnS_2.

Scheme for analysis—

Wash the residue well with hot water and proceed as follows:

1. Note the **colour** of the washed residue.

2. Perform the **Preliminary tests (for basic radicals)** especially the following:

(*i*) Cobalt nitrate test for white residue.
(*ii*) Borax bead test for coloured residue.
(*iii*) Flame test.
(*iv*) Special test (fusion test) for green residue.
(*v*) Fluorescent test for SnO_2.

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*$PbCl_2$ goes in solution upon boiling with water but reappears on cooling.

†The solubility of $CaSO_4$ in dil. HCl is such as it can be detected in the same acid solution during the usual course of an analysis in the wet-way.

‡ Sb_2O_4 is very slowly attacked by conc. HCl. Both Sb_2O_4 and Fe_2O_3 undergo dissolution by prolonged boiling with conc. HCl.

§ Silver halides turn violet on exposure to light.

3. Perform only the following preliminary tests for acidic radicals:

(*i*) Warming the residue with conc. H_2SO_4.

(*ii*) Warming the residue with MnO_2 and conc. H_2SO_4.

(*iii*) Special test for silicate.

4. Examine the insoluble residue in the wet way either by the (*a*) General method *or*, by (*b*) Special methods.

1. Colour

As the insoluble compounds are very few in number, the colour of the residue gives some idea about the nature of the substance to be sought for and may act as a guide as to the experiments, which are to be carried out in the next step. For example, it is no use of performing the cobalt nitrate test, if the residue be coloured; but borax bead test, on the other hand, should be performed.

2. Preliminary tests for basic radicals

Perform the preliminary tests more or less in the order given below:

Experiments	Observations	Inferences
(*i*) Closed Tube Test	(*a*) The substance does not change.	Sulphates of Pb, Ba, Sr and Ca; Al_2O_3 CaF_2, SiO_2 and silicates; chrome iron ore and $PbCrO_4$.
	(*b*) Yellow when hot, white when cold.	SnO_2, Sb_2O_4.
	(*c*) The substance melts to a yellow liquid and then gives a white sublimate.	$PbCl_2$

Experiments	Observations	Inferences
(*ii*) Charcoal Test in oxidising flame.	(*a*) White residue	Sulphates of Ba, Sr and Ca; Al_2O_3, CaF_2, SiO_2 and Silicates.
	(*b*) Brown residue	Fe_2O_3, chrome iron ore; $PbCrO_4$.
	(*c*) Green residue	Cr_2O_3.
(*iii*) If the original residue is white and a white residue is left on charcoal in the expt. (*ii*) above, perform *Cobalt Nitrate Test.*	Blue residue	Al_2O_3,SiO_2 and silicates.
(*iv*) If the original insoluble residue is coloured and a coloured residue is left on charcoal in the expt.(*ii*) above, apply *Borax Bead Test.*	(*a*) A green bead in both O. F. and R.F.	Cr_2O_3, chrome iron ore; $PbCrO_4$.
	(*b*) Bead turns yellow in O.F. & bottle green in R.F.	Fe_2O_3.
(*v*) Subject the insoluble residue to charcoal reduction test after mixing it with Na_2CO_3 and KCN.	(*a*) Malleable bead, which marks paper.	Pb-compounds
	(*b*) Bead does not mark paper.	Ag, Sn and Sb compounds.
(*vi*) Flame test [Heat a little of the'insoluble'on a pt.-wire, first in the reducing zone of the flame, then moisten it with conc. HCl by dipping the wire in the acid and heat again in the non-luminous flame.]	(*a*) Permanent crimson.	Sr
	(*b*) Brick-red and transient.	Ca
	(*c*) Yellowish-green	Ba

Experiments	Observations	Inferences
(*vii*) Microcosmic salt bead test.	A skeleton[1] bead	SnO_2, Silica and silicates
(*viii*) Special test, *i.e.*, oxidising fusion test, if the insoluble residue be green in colour (*see* page 20).	The mass turns yellow.	Cr_2O_3
(*ix*) *Fluorescent test for tin.* Take in a small beaker about 0·25 gm. of the insoluble residue, add sufficient dil. HCl (1:1) & a piece of zinc. Stir the mixture with a clean test tube half filled with water. Withdraw the test tube and hold it quickly in the non-luminous Bunsen flame.	A fluorescence[2] (*i.e.*, beautiful azure glow) on the outer side of the test-tube.	SnO_2

3. Preliminary tests for acidic radicals

The anions that may remain associated with the insoluble residue are:
S'', SO_4'', SiO_3'', F', Cl', Br', I' and CrO_4'', one or more of which may be found in the insoluble residue.

Notes: 1. A negative result is no definite proof of the absence of silica and silicates.

2. The test is extremely sensitive. The reagents to be used must be free from tin-compounds. Hence, a blank experiment should always be carried out with zinc and HCl to be used, before performing the test with unknown substance.

Perform the following experiments more or less in the order given below:

Experiments	Observations	Inferences
(*i*) Warming of the insoluble with conc. H_2SO_4.	The gas evolved turns a drop of water on the glass rod turbid.	Fluoride (*i.e.*, CaF_2 is indicated).
(*ii*) Warming of the insoluble with MnO_2 and conc. H_2SO_4.	Evolution of chlorine, bromine and iodine, having characteristic colours (*see* page 26).	Insoluble halides (*i.e.*, AgCl, AgBr, AgI and may be $PbCl_2$ also).
(*iii*) Silicon tetrafluoride test (*see* special tests for acids, page 30).	A wax-like deposit on drop of water.	Silicate or silica.

4. Examination of the insoluble residue in the wet-way

Some idea about the nature of the 'insoluble residue' being obtained from the above tests, **special methods** (which in some cases of insoluble residues are cartainly advantageous) for analysing the same may be adopted. But in the case of a mixture of several insolubles, and, in fact, to be more systematic in every case, the following **general method** should be followed:

Fuse the residue by mixing with 4-5 times of fusion mixture (or, Na_2CO_2+a few beads of NaOH) in a nickel* crucible (or on a mica foil, if nickel crucible be not available) to a clear melt. Keep the mass in molten condition for ten minutes. Cool and transfer into a beaker, boil with water and filter.

---

*Note that molten alkali carbonate attacks nickel crucible and nickel oxide is formed. This may be found in the analysis.

N.B. Moreover, before entering into the actual procedure (fusion) lead and silver compounds should be looked for in the insoluble residue—a drop of alkaline sulphide turns them black.

<table>
<tr><th>Residue:</th><th colspan="3">Filtrate:</th></tr>
<tr><td rowspan="3">May contain (<i>i</i>) some insoluble carbonates (carbonates of Ba, Sr, Ca and basic lead carbonate); (<i>ii</i>) some unreacted CaF_2, Fe_2O_3, Al_2O_3, SnO_2, Sb_2O_4 etc.
Extract with dil. HCl, filter and examine the filtrate for metals from Gr. II according to general group separation table. [But if Pb and/or Ag be present, extract with minimum volume of dil. HNO_3. Filter and evaporate the filtrate nearly to dryness. Evaporate finally on water bath, extract with cold water. Examine the solution from Group I for metals according to general group separation table.]</td><td colspan="3">May contain: (<i>i</i>) acid part of the insoluble residue as Na-salt (and corresponding K-salt if fusion mixture be employed); (<i>ii</i>) excess of added reagents and (<i>iii</i>) metals of Groups II and III. Divide the filtrate into <i>two</i> parts.</td></tr>
<tr><td rowspan="2">Examine one part for anions as usual.
Anions to be looked for; S'', SO_4'', F', Cl', Br', I' and CrO_4''.</td><td colspan="2">Examine the other portion for metals of Grs. II and III. But if silica or silicates be previously detected, acidify the solution with conc. HCl, evaporate to dryness. Moisten the residue with conc. HCl and evaporate again to dryness. Repeat the process once or twice and bake the residue for 15 minutes. Cool and extract with dil. HCl by warming, if necessary. Filter.</td></tr>
<tr><td>Residue:
May contain SiO_2. (may be confirmed by SiF_4 test).</td><td>Filtrate:
(<i>i</i>) With a little of the filtrate test for SO_4''. (<i>ii</i>) Examine the remaining portion for metals of Grs. II and III.</td></tr>
</table>

Special Methods of treating the Insoluble Residue

(*a*) *Ignited* SnO_2. If the colour of the rssidue be white and tin be suspected in the preliminary tests carried out with the insoluble residue, the following method may be adopted:

Mix the residue with about 5-6 times its weight of a mixture of sulphur and anhydrous sodium carbonate. Take the mixture in a porcelain crucible; cover it with a lid and heat over a small flame till the excess of sulphur burns away. Cool, extract with hot water and filter. Acidify the filtrate with dil. HCl, a *yellow ppt.* of SnS_2 indicates the presence of SnO_2 in the sample. Confirm tin by performing the usual tests (*see* Table 6, page 61) with this yellow ppt.

Reactions.—Tin dioxide on reaction with sulphur and Na_2CO_3 is converted into soluble sodium thiostannate, the solution of which on acidification gives a yellow ppt. of SnS_2

$$2SnO_2+2Na_2CO_3+9S=2Na_2SnS_3+3SO_2+2CO_2;$$
$$Na_2SnS_3+2HCl=SnS_2+H_2S+2NaCl$$

(*b*) *$PbSO_4$, $PbCl_2$*. If the colour of insoluble residue be white and lead be previously suspected in the preliminary tests, treat the residue in the following way:

Take about 5 c.c. of a concentrated solution of ammonium acetate. Make it slightly acidic by adding dil. acetic acid. Add this acidic solution to a portion of the residue, shake and heat to about 70°C and filter. Divide the fitrate into *three* parts.

Part I:	**Part II:**	**Part III:**
Dilute with water and add a little K_2CrO_4 solution—a *yellow ppt.* indicates *Lead.*	Dilute much with water to avoid precipitation of silver acetate and add $AgNO_3$ solution—*a white ppt. soluble* in NH_4OH indicates *Chloride.*	Dilute with water and then add a solution of $Ba(NO_3)_2$, when a heavy *white ppt. insoluble* in excess of HCl indicates *Sulphate.*

N.B. (*i*) Note that ionisation of $Pb(C_2H_3O_2)_2$ in presence of an excess of acetate ions occurs only to a very small extent. The formation of lead acetate is explained by the following equation:

$$PbSO_4+2C_2H_3O_2{}' \rightleftharpoons Pb(C_2H_3O_2)_2+SO_4{}''.$$

(*ii*) The above method is of great importance in separating $PbSO_4$ from $BaSO_4$, silica, etc., which remain insoluble in ammonium acetate.

(c) Chromite ($FeCr_2O_4$), strongly ignited oxides of Sn, Fe, Al and Cr. Sufficient indication about the presence of these substances will have been obtained from the preliminary tests carried out with the insoluble residue. In case any of the above substances is suspected, the following method of attacking the residue may be adopted:

Heat about 0·2g. of the substance with 5 times its weight of sodium peroxide in a nickel crucible to fusion for 20 minutes. Dissolve in water. Boil to destroy hydrogen peroxide and filter.

Residue:	**Filtrate:**
Brown $Fe(OH)_3$. Dissolve in dil. HCl. and divide the solution into *two*: (*i*) To one portion add KCNS solution —*a blood-red* coloration confirms *Iron.* (*ii*) To another portion add $K_4Fe(CN)_6$ solution—*a deep-blue* precipitate or coloration confirms *Iron.*	(*i*) If *yellow.* CrO_4'' ions present, confirm by usual tests. If colourless, it need not be further tested for. (*ii*) Through another portion of the filtrate pass H_2S and then acidity with very dil HCl ; *a yellow ppt.* indicates *Tin.* Confirm tin by performing usual test with this *yellow ppt.* (*see* Table 6 page 61). (*iii*) Boil another portion of the solution with 1-2 gms. of soid NH_4Cl till a faint odour of ammonia persists —*white gelatinous ppt.* confirms *Aluminium.*

(d) Ignited oxides of Fe, Al and Cr in presence of SiO_2. If SiO_2 and any of the above-mentioned compounds be previously suspected in the insoluble residue, the following method may be followed:

Heat fused acid potassium sulphate preferably in a silica crucible (in its absence use porcelain crucible) over a small flame. As soon as the frothing has ceased, add the dry residue (about $\frac{1}{12}$th. of the amount of acid sulphate), continue gentle heating till the melt begins to solidify, then raise the temperature and continue heating till the melt is completely clear. Cool and extract with dil. H_2SO_4. Examine the resulting solution as usual for the above-mentioned cations. SiO_2, if present, remains insoluble.

N.B. (*i*) Acid potassium sulphate, when heated first melts and then at about 300°C loses water and is converted into pyrosulphate. $2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$.

Cessation of frothing indicates that this conversion of acid potassium sulphate into pyrosulphate is complete. Pyrosulphate, when heated again, is converted into normal sulphate giving off SO_3, which is highly active at hight temperature. $K_2S_2O_7 \rightarrow K_2SO_4 + SO_3$. When the reaction is complete, the melt contains K_2SO_4 and sulphates of the above-mentioned metals. $3K_2S_2O_7 + Al_2O_3 \rightarrow Al_2(SO_4)_3 + 3K_2SO_4$.

(*ii*) Aluminium silicate also is often treated by this method.

(*e*) *Fused* $PbCrO_4$. If the insoluble substance is brown in colour and if Pb and Cr be suspected in the preliminary tests, then the insoluble residue, in all probability, contains $PbCrO_4$. The residue may be examined in the following way:

Fuse the solid residue with NaOH on a mica foil (preferably in a nickel crucible), keep the mass in fused state for 5 minutes and extract with hot water. Filter and concentrate the filtrate to a small volume by boiling. Add an excess of conc. HCl, boil vigorously and evaporate *almost* to dryness. Cool, dilute with water and filter.

Residue:	**Filtrate:** Warm and pass H_2S till saturation. Filter.	
(White) $PbCl_2$ Dissolve by boiling with water and add K_2CrO_4 solution to it. Cool, —a yellow ppt. confirms *Lead*.	**Residue:** (Black) PbS Confirm, if necessary, by performing the usual tests with this ppt.	**Filtrate:** Boil off H_2S from the filtrate. Precipitate chromium by adding Gr. IIIA reagents. Confirm chromium as usual by carrying out tests with this ppt. (*see* Table 7, p. 63).

Reaction: When fused lead chromate is boiled with NaOH solution, it dissolves.

$$PbCrO_4 + 4NaOH = Na_2CrO_4 + Na_2PbO_2 + 2H_2O.$$

(*f*) *AgCl, AgBr* and *AgI.* If the insoluble residue be white or light yellow in colour and if silver be indicated in the preliminary dry test, the following method may be tried:

Add a little dil. H_2SO_4 to the residue. Then add a piece of zinc in such a manner so that it remains in contact with both acid and the insoluble mass. Warm and allow to stand for sometime. Filter (or pour off the acid).

Residue:	**Filtrate:**
Spongy mass of metallic silver. Wash with water, dissolve in dil. HNO_3. Filter, if necessary, and add dil. HCl to the filtrate—a *curdy-white ppt.* insoluble in excess of dil. HNO_3 but soluble in dil. NH_4OH solution indicates *Silver.*	To a portion of the filtrate add $AgNO_3$ solution. If a *white or yellow ppt.* insoluble in excess of dil. HNO_3 is obtained, examine the remaining portion of the filtrate for chloride, bromide and iodide in the usual way.

N.B. By placing the silver halide in contact with zinc in presence of dil. acid, silver halide is readily reduced to metallic silver. $AgX+H \rightarrow Ag+HX$ (where X stands for halogen).

Specimen Records of Analytical Results

Sample No......

Date......

A white powder, one part of which was soluble in dil. HCl and the rest resisted all the attacks by other solvents including *aqua regia.*

Preliminary tests for basic radicals

Experiments	Observations	Inferences
1. A small quantity of the sample was heated in a clean and dry test-tube.	No change at all	May be Al, Ba, Ca, Sr, Mg.
2. A small portion of the sample was heated in a cavity on charcoal block in O.F.	A white residue	A large variety of substances.
3. The residue was moistened with a drop of cobalt nitrate and heated again in O.F.	Blue residue	Al-compounds, PO_4''', borate, arsenate, silicate.
4. A portion of the sample was mixed with anhydrous Na_2CO_3 and heated on charcoal in R.F.	Incandescent on heating.	Ba, Sr, Ca, Mg, Al, Si.
5. A little of the sample moistened with conc. HCl was heated on pt.-wire in a non-luminous flame.	No characteristic flame.	Cu, Ca, Ba, Sr, etc. absent.
6. A small portion of the sample was heated on microcosmic bead.	No characteristic change	Co, Cu, Silica, Silicates, SnO_2, etc. may be absent.

Preliminary tests for acid radicals

Experiments	Observations	Inferences
1. To a portion of the sample in a test-tube dil. HCl was added and finally warmed.	No characteristic change.	CO_3'', SO_3'', S_2O_3'' etc. absent.
2. The above expt. was repeated by using conc. H_2SO_4 instead of dil. HCl.	No characteristic change.	F′, Cl′, Br′, I′, NO_2', etc. absent.

Experiments	Observations	Inferences
3. A portion of the sample was warmed with conc. H_2SO_4 & MnO_2.	No gas or vapours evolved.	Cl′, Br′, I′ absent.
4. A portion of the sample was warmed with conc. H_2SO_4 and copper turnings.	No brown fumes	NO_3', NO_2', Br′ absent.

Some special tests for acid radicals

Experiments	Observations	Inferences
1. A portion of the sample was heated with 1:1 HCl and a few granules of zinc. A moist lead acetate paper was then held at the mouth of the test-tube.	No blackening of lead acetate paper.	S″ absent
2. A few drops of a solution of the sample in dil. HNO_3 was added to an excess of ammonium molybdate containing HNO_3 and finally warmed.	A canary yellow ppt.	May be phosphate, arsenate.
3. To a paste of the substance with conc. H_2SO_4 1 c.c. methyl alcohol was added. The mixture was then heated and the issuing gas ignited.	No green-edged flame.	Boric acid, borate absent.
4. A portion of the sample was heated with CaF_2 and conc. H_2SO_4 in a lead basin and a pt.-loop carrying water was held over the opening of the lid.	No turbidity	Silica, silicate absent.

Wet tests for basic radicals

A portion of the sample was boiled with dil. HCl and filtered. With the filtrate the group analysis is carried out as follows. Since no ppt. came down on cooling, Gr.-1 elements were absent. A portion of the filtrate was warmed and H_2S passed through, it was then diluted with water and H_2S was passed again till saturation.

<table>
<tr><td rowspan="6">No ppt.
Gr.-II
elements
absent</td><td colspan="6">To the main portion of the filtrate a few drops of conc. HNO_3 was added and boiled. A little of this solution was tested with ammonium molybdate—a canary yellow ppt. confirmed Phosphate. Another small portion of this solution was tested for iron with NH_4SCN—no blood-red coloration confirming the absence of iron.
To the main bulk solid NH_4Cl was added and boiled. Dil. NH_4OH was then added dropwise till permanent turbidity. It was boiled and diluted. 2-3 c.c. dilute acetic acid and about 20 c.c. of a saturated solution of ammonium acetate were added. It was then boiled.</td></tr>
<tr><td rowspan="5">No ppt.</td><td colspan="5">To the hot solution freshly prepared neutral ferric chloride solution was added dropwise stirring the hot solution all the time, till the solution assumes the cream colour of a light tea. It was boiled for a minute and filtered hot.</td></tr>
<tr><td rowspan="4">Residue:
Rejected</td><td colspan="4">Filtrate:
A little of the filtrate was tested with a drop of $FeCl_3$—no yellow ppt.—indicating that phosphate has been completely removed. The main portion of the filtrate was heated to boiling and NH_4OH was added in slight excess &amp; filtered.</td></tr>
<tr><td rowspan="3">Residue: A portion of this residue was dissolved in 1 : 1 HNO_3 and boiled gently with Pb_3O_4 for about a minute. It was then diluted with water and allowed to settle—No pink or violet colour—Manganese absent.</td><td colspan="3">Filtrate*: A little portion of it was slightly warmed and H_2S passed through.</td></tr>
<tr><td rowspan="2">No ppt.
Gr.-IIIB
elements
absent</td><td colspan="2">The main portion of the above filtrate* was concentrated to 1/4 of its bulk. A little NH_4OH was added and then saturated $(NH_4)_2CO_3$ solution was added, warmed and allowed to stand.</td></tr>
<tr><td>No ppt.
Gr.-IV
elements
absent</td><td>To the solution Na_2HPO_4 solution was added. It was then shaken and the inside of the test-tube was scratched— white crystalline ppt. confirms Magnesium.</td></tr>
</table>

Wet tests for acid radicals

A portion of the substance was boiled with Na_2CO_3 and water and then filtered. With the filtrate the following wet reactions were carried out:

Experiments	Observations	Inferences
1. To a little of the prepared solution a few drops of sod. nitroprusside solution was added.	No pink or violet colour.	Sulphide absent.
2. A little of the prepared solution was neutralised with dil. HCl, CO_2 boiled off and $BaCl_2$ soln. added.	No ppt.	Sulphate absent.
3. A portion of the prepared solution was neutralised with dil. HNO_3, CO_2 boiled off and $AgNO_3$ solution was added.	No ppt.	Cl′, Br′, I′ absent.
4. A portion of the solution was acidified with dil. HNO_3, CO_2 boiled off. NH_4OH was then added to make the solution just alkaline, the excess ammonia was then boiled off. To the neutral solution a freshly prepared dil. soln. of $FeCl_3$ was added.	No blood-red colour but a yellow ppt. insoluble in dil. HAc. but soluble in dil. mineral acid came down.	Thiocyanate absent. May be phosphate.

Confirmation of the suspected acid

To a portion of Na_2CO_3 extract dil. HCl was added till faintly acid and CO_2 boiled off. The solution was then made alkaline by adding NH_4OH. Excess of magnesia mixture was added to it and let stand for a few minutes and filtered.

Filtrate: Acidified with dil. HCl & H_2S was passed—no yellow ppt.—arsenite absent.	**Residue:** Washed with water, dissolved in dil. HCl, H_2SO_3 added, the excess of which was boiled off. H_2S was then passed.	
	No ppt. arsenate absent.	H_2S was boiled off. Conc. HNO_3 was added and a few drops of it was added to an excess of ammon. molybdate solution containing 2-3 c.c. conc. HNO_3. The mixture was shaken and finally warmed —a canary yellow ppt. confirms *Phosphate.*

HCl-soluble portion of the sample therefore contains Mg^{++} as basic radical and PO_4''' as acid radical.

Treatment of insoluble residue

The residue was white in colour.

Preliminary tests for basic radicals

Experiments	Observations	Inferences
1. A portion was heated on charcoal in O.F.	White residue	May be sulphates of Ba, Sr & Ca; Al_2O_3, CaF_2, SiO_2 and silicates.
2. The residue was moistened with a drop of cobalt nitrate and heated again in O.F.	Blue residue	Al_2O_3, SiO_2 and silicates.
3. A little of the residue was first heated on pt. -wire in the reducing zone of the flame, then moistened with conc. HCl and heated again in the non-luminous flame.	No characteristic colour.	Ba, Ca, Sr absent.
4. A portion of the insoluble residue was treated with 1 : 1 HCl and zinc. The mixture was stirred with a test-tube half filled with water. The test-tube was then quickly held over a non-luminous flame.	No fluorescence	Absence of SnO_2.

Preliminary tests for acid radicals

Experiments	Observations	Inferences
1. Warming of the insoluble with conc. H_2SO_4.	No characteristic change.	F′ absent
2. Warming of the insoluble with MnO_2 and conc. H_2SO_4.	No gas or vapours evolved.	Cl′, Br′, I′ absent.
3. Silicon tetrafluoride test (as already described).	No turbidity of water drop.	Silica, Silicate absent.

Hence the insoluble residue is in all probability Al_2O_3.

Wet tests

This insoluble residue was heated to fusion with 5 times its weight of sodium peroxide in a nickel crucible. It was then treated with water, boiled and filtered. A portion of the filtrate was then boiled with solid NH_4Cl till a faint odour of ammonia persists—a white gelatinous ppt. confirms *Aluminium*.

$\therefore$ the insoluble residue is Al_2O_3

Hence, the composition of the sample:

$Mg_3(PO_4)_2$, Al_2O_3.

Sample No.........

Date.........

A black powder, one part of which was soluble in water and the rest in conc. HCl on prolonged boiling.

Preliminary tests for basic radicals

Experiments	Observations	Inferences
1. A small portion of the sample was heated in a clean and dry test tube.	The substance got fused.	May be compounds of alkali and alkaline earth metals.
2. A small portion of the sample was heated in a cavity on charcoal block in O.F.	Decrepitation occurred.	Bromides, iodides, etc. of alkalis, crystalline salts, etc
3. A portion of the sample was mixed with anhydrous Na_2CO_3 and heated on charcoal in R.F.	No characteristic change	
4. A little of the sample was heated on borax bead first in oxidising and then in reducing flame.	Amethyst violet in O.F. but colourless in R.F.	May be Mn compounds.
5. A little of the sample moistened with conc. HCl was heated on a pt. wire in a non-luminous flame.	Light violet in naked eye but intense violet red through blue glass.	Potassium compound.
6. Fusion test for Mn & Cr was carried out with NaOH and KNO_3.	A green mass	Mn compound
The solution of the green mass in water was acidified with dil. HNO_3.	A pink colour developed.	

Preliminary tests for acid radicals

Experiments	Observations	Inferences
1. A portion of the sample was treated with dil. HCl first in the cold and then on warming.	No change	CO_3'', SO_3'', S_2O_3''. etc. absent.
2. The above expt. was repeated by using conc. H_2SO_4 instead of dil. HCl.	A reddish brown gas evolved. The evolved gas turned CS_2 brown.	May be Br', NO_2' and NO_3'. May be Br'
3. A small portion of the sample was warmed with conc. H_2SO_4 and MnO_2.	Evolution of reddish brown gas.	May be Br'
4. A small portion of the sample was warmed with conc. H_2SO_4 and copper turnings.	Evolution of brown fumes.	May be NO_2'. NO_3', Br'.

Some special tests for acid radicals

Experiments	Observations	Inferences
1. A portion of the sample was heated with 1:1 HCl and a few granules of zinc. A moist lead acetate paper was held at the mouth of the test-tube.	No blackening of lead acetate paper.	S''—absent
2. A few drops of a solution of the sample in dil. HNO_3 was added to an excess of ammon. molybdate containing HNO_3 and finally warmed.	No yellow ppt.	Phosphate, arsenate absent.
3. To a paste of the substance with conc. H_2SO_4 1 c.c. methyl alcohol was added. The mixture was then heated and the issuing gas ignited.	No green-edged flame.	Boric acid, borate absent.
4. Aportion of the sample was heated with CaF_2 and conc. H_2SO_4 in a lead basin and a pt.-loop carrying water was held over the opening of the lid.	No turbidity of water drop.	Silica and Silicate absent.

Wet tests for basic radicals: Analysis of water extract

A portion of the sample was boiled with water and filtered. With the filtrate the group analysis is carried out as follows:

To the filtrate dil. HCl was added dropwise.

<table>
<tr><td rowspan="7"><i>No. ppt.</i>
Gr.-I
absent</td><td colspan="7">A little of the above acidified solution is heated to boiling and H_2S was passed till saturation.</td></tr>
<tr><td rowspan="6"><i>No. ppt.</i>
Gr.-II
absent</td><td colspan="6">To the main bulk of the solution solid NH_4Cl was added and boiled. Dil. NH_4OH was then added dropwise till ammoniacal.</td></tr>
<tr><td rowspan="5"><i>No. ppt.</i>
Gr.-IIIA
elements absent</td><td colspan="5">The solution was warmed and H_2S passed through.</td></tr>
<tr><td rowspan="4"><i>No. ppt.</i>
Gr.-IIIB
elements absent</td><td colspan="4">Acidified with HAc. H_2S was then boiled off and the solution concentrated to 1/4 of its bulk. A little NH_4OH was added and a saturated solution of $(NH_4)_2CO_3$ added in slight excess, warmed, allowed to stand.</td></tr>
<tr><td rowspan="3"><i>No. ppt.</i>
Gr.-IV
elements absent</td><td colspan="3">The solution was divided into <i>two</i> parts.</td></tr>
<tr><td rowspan="2">To one part Na_2HPO_4 solution was added. It was then shaken and the inside of the test-tube scratched;—no ppt. -Mg absent.</td><td colspan="2">The other portion was evaporated to dryness and the residue heated till the evolution of white fumes ceases. It was again heated to dryness with conc. HNO_3 and the residue further heated. The residue was taken up with about 3 c.c. of water and divided into <i>two</i> parts.</td></tr>
<tr><td>To one part a little acetic acid and freshly prepared sodium cobaltinitrite solution was added —A yellow ppt. of $K_2Na\ [Co(NO_2)_6]$ confirmed <i>Potassium.</i></td><td>To the other part a little of potassium antimonate solution was added and the inside of the test-tube scratched.-No crystalline white ppt.—sodium absent.</td></tr>
</table>

A little of the original sample was heated with sodalime and filter paper soaked with mercurous nitrate solution was held at the mouth of the test-tube.—No smell of ammonia and the mercurous nitrate paper did not turn black—NH_4^+ absent.

Analysis of HCl extract

The residue left over after the treatment of the sample with water was dissolved in conc. HCl by prolonged boiling.

The solution was cooled and diluted with water.

<table>
<tr><td rowspan="5"><i>No. ppt.</i> Gr.-I elements absent</td><td colspan="5">A little of the solution was warmed and H_2S was passed through till saturation.</td></tr>
<tr><td rowspan="4"><i>No. ppt.</i> Gr.-II elements absent</td><td colspan="4">To the main bulk of the solution solid NH_4Cl was added and boiled. Dil NH_4OH was then added dropwise till ammoniacal.</td></tr>
<tr><td rowspan="3"><i>No. ppt.</i> Gr.-IIIA elements absent</td><td colspan="3">The solution was warmed, H_2S passed through and filtered.</td></tr>
<tr><td rowspan="2"><i>Flesh coloured ppt.</i> Gr.-IIIB elements present</td><td colspan="2">Filtrate: Acidified with HAc. H_2S was then boiled off and the solution concentrated to 1/4 of its bulk. A little NH_4OH was added and a saturated solution of $(NH_4)_2CO_3$ added in excess, warmed, allowed to stand.</td></tr>
<tr><td><i>No ppt.</i> Gr.-IV elements absent</td><td>To the solution Na_2HPO_4 solution was added. It was then shaken and the inside of the test-tube scratched. No precipitate indicating absence of Mg^{++}</td></tr>
</table>

Treatment of IIIB ppt.

The ppt. was washed and treated with dil. HCl (1 : 10).

<table>
<tr><td rowspan="2">No residue: Nickel and cobalt absent</td><td colspan="2">H_2S was boiled off from the solution. It was then cooled and treated with an excess of NaOH solution and filtered.</td></tr>
<tr><td>Filtrate: Through the filtrate H_2S was passed. —No ppt., zinc absent.</td><td>Residue:
(<i>i</i>) It was dissolved in 1 : 1 HNO_3 and about 1 gm. of Pb_3O_4 added. It was boiled for a minute, diluted with water and allowed to stand—a pink colour confirming the presence of <i>Manganese</i> developed.
(<i>ii</i>) Oxidising fusion test —Manganese.</td></tr>
</table>

Wet tests for acid radicals : Examination of water extract

No heavy metal being present in water extract it was directly analysed.

Experiments	Observations	Inferences
1. A little of the water extract was made alkaline with NaOH solution and a few drops of sodium nitroprusside added.	No violet colouration.	S″ absent
2. A little of the water extract was acidified with dil. HCl and then $BaCl_2$ solution added.	No ppt.	SO_4'' absent
3. A portion of water extract was acidified with dil. HNO_3 and then $AgNO_3$ solution added.	A pale yellowish ppt. soluble in excess of NH_4OH.	May be Br′
4. Ring test with $FeSO_4$ solution and conc. H_2SO_4 was performed.	Brown ring at the junction of liquid layers.	Br′, NO_3', NO_2'
5. A portion of the aqueous solution was warmed with NaOH and aluminium powder.	No smell of ammonia.	NO_3', NO_2' —absent.
6. A portion of water extract was acidified with dil. H_2SO_4 and 1 c.c. of CCl_4 added. Chlorine water was then added in drops and the test-tube shaken after each addition.	Carbon tetrachloride layer turned reddish-brown.	Br′ confirmed
7. To a little of water extract $FeCl_3$ was added.	No red coloration.	Thiocyanate absent.

Examination of acid in water-insoluble portion

A portion of the sample which remained undissolved in water was boiled with water and sodium carbonate and then filtered. With the filtrate the following wet reactions were carried out:

Experiments	Observations	Inferences
1. To a little of the prepared soln a few drops of sodium nitroprusside solution was added.	No coloration	S″ absent
2. A little of the prepared solution was acidified with dil. HCl, CO_2 boiled off and $BaCl_2$ solution added.	No ppt.	SO_4'' absent
3. A portion of the prepared solution was acidified with dil. HNO_3, CO_2 boiled off and $AgNO_3$ solution added.	No ppt.	Cl′, Br′, I′ absent.
4. A portion of the prepared solution was acidified with dil. HNO_3 and CO_2 boiled off. The solution was then neutralised with NH_4OH and $FeCl_3$ solution was added in drops.	No ppt. No red colour.	Phosphate, thiocyanate absent.

Conclusion: In water-soluble portions of the sample there was only potassium as basic radical and bromide as acidic radical. Hence, the water-soluble portion was potassium bromide.

In water-insoluble portion of the sample there was manganese as basic radical. No acid radical being found manganese was present probably as oxide. Moreover, the sample was black in colour and on heating the sample with conc. HCl a greenish-yellow gas having irritating smell and blueing starch-potassium iodide paper evolved. Hence, the water-insoluble portion was manganese dioxide. The sample was therefore a mixture of KBr and MnO_2.

PART II

ORGANIC QUALITATIVE ANALYSIS

EXAMINATION OF ORGANIC COMPOUNDS

1. CLASS DETERMINATION

CHAPTER 1

SCHEME

The first step in qualitative organic analysis is to ascertain the constituent elements present in the compound supplied. Organic compounds must always contain carbon. Hydrogen and oxygen are often present as constituents of an organic compound. Besides the above elements, an organic compound may contain one or more of the following elements: *Nitrogen*, *halogens* (chlorine, bromine and iodine), *sulphur*, *phosphorus*, *arsenic*, *magnesium*, etc. But carbon, it should be noted, is to be tested for only when a compound is not definitely known to be organic. Evidently such a case does not arise here. The test for hydrogen is not worthwhile, as the detection is time-consuming and the few common organic substances that contain no hydrogen present no special difficulty in detection. The presence of oxygen is usually inferred by the recognition of functional groups, *e.g.*, $>\mathrm{CO}$, $-\mathrm{OH}$, $-\mathrm{COOH}$ etc. Hence considering the above facts and keeping in view the limitations of the syllabus, *nitrogen*, *sulphur* and *halogens* only are to be looked for.

The next step is to detect the functional groups (*i.e.*, groups which determine the chemical behaviour of a compound) present in the compound.

Hence the qualitative analysis (as per syllabus) of an organic compound involves:

1. **Detection of elements:** such as nitrogen, sulphur and halogens (chlorine, bromine and iodine).

2. **Detection of functional groups** *e.g.*, $-\mathrm{OH}$, $-\mathrm{COOH}$ etc.

CHAPTER II

DETECTION OF ELEMENTS

A. Lassaigne's method:

Take a pea-size piece of clean sodium in a clean and dry ignition tube and carefully heat over a flame to melt it. Now add in portions the substance under investigation over molten sodium. Heat the tube again very strongly till red hot. Carefully immerse the tube into 20 c.c. distilled water, taken in a porcelain mortar; break the tube by tapping, if necessary. Grind up the broken glass pieces and the fused mass thoroughly with a pestle. Filter the mixture and perform the following experiments, taking a portion of the filtrate at a time.

Experiments	Observations	Inferences
(*i*) To a portion of the filtrate add a few drops of freshly prepared ferrous[1] sulphate solution.	A black ppt.	May be sulphur.
Should no black ppt. appear, boil the mixture for about a minute (but if a black ppt. appears, add a little more of ferrous sulphate solution and then boil), cool, acidify with conc. HCl and then add one or two drops of ferric chloride solution.	A deep[2]-blue ppt. or coloration.	Nitrogen
(*ii*) To a little of the filtrate add a drop of freshly prepared sodium nitroprusside solution.	A violet coloration (transient).	Sulphur
(*iii*) Acidify a little of the filtrate with dil. HNO_3 and add $AgNO_3$ solution.	A white[4] or yellow ppt.	Chlorine, Bromine and Iodine (one or more than one elements).
N.B. If either nitrogen or sulphur (or both) be present, boil[3] a portion of the filtrate with an *excess* of dil. HNO_3 and then cool before the addition of $AgNO_3$ solution.		

Experiments	Observations	Inferences
(*iv*) If a ppt. be obtained in expt. -(*iii*), acidify strongly a little of the filtrate (obtained from sodium fusion) with dil. H_2SO_4 or dil. HCl; add 1-2 c.c. of CCl_4 (or CS_2). Now add strong chlorine water drop by drop and shake after each addition.	The CCl_4 (or CS_2) layer turns— (*a*) violet; (*b*) brown or reddish-brown.	 (*a*) Iodine (*b*) Bromine
If CCl_4 (or CS_2) layer be violet, continue addition of chlorine water dropwise and shake after each addition.	(*a*) Violet colour disappears and a reddish-brown colour appears.	Both iodine and bromine.
	(*b*) CCl_4 (or CS_2) layer becomes colourless after the disappearance of violet colour.	Iodine but **no** bromine.
	(*c*) No violet or brown colouration at all.	May be chlorine.
(*v*) If no violet or brown colour be developed in expt. -(*iv*) treat the ppt. obtained in expt. -(*iii*) on addition of $AgNO_3$ solution with dilute NH_4OH solution. **N.B.** For detecting chlorine in presence of other halogen elements perform the 'additional tests' described towards the end of this chapter.	The ppt. readily dissolves.	Chlorine

B. Middleton's method (alkali zinc test):

Mix pure zinc dust with about half its weight of pure and anhydrous sodium carbonate. Place a little of the solid[5] organic substance under investigation inside an ignition tube. Cover it up with a layer of (about 3 cm. thickness) the prepared mixture. Shake the tube well after fitting it up with a cork. Remove the cork and add a little of the mixture (Na_2CO_3+Zn dust) again, start heating from the upper portion and extend gradually downwards. Heat at first gently and then strongly till the tube becomes red hot. Now plunge the tube into 20 c.c. distilled water contained in a mortar. Grind up the broken test-tube and filter. Examine the filtrate for nitrogen and halogens as described under Lassaigne's method. In order to test for 'sulphur', treat the residue that remains on the filter paper with dil. HCl. If sulphur be present, H_2S (characterised by rotten egg-like smell) is evolved.

C. Beilstein's test for halogens:

Heat a piece of stout copper wire in the non-luminous Bunsen flame until it ceases to colour the flame green. Allow it to cool and then touch the substance with the end of the wire and heat again in the flame. A *green* colour of the flame *indicates* the presence of **halogen**[6].

Notes on detection of elements

1. *Ferrous sulphate solution*:

Wash a few crystals of ferrous sulphate with water and then dissolve the washed crystals in water.

2. *Reactions occurring in the detection of elements*:

During fusion nitrogen of the organic compound combines with carbon and sodium to give sodium cyanide, while sulphur and halogens, if present, combine with sodium giving sodium sulphide and sodium halide respectively.

$$Na+C+N = NaCN$$
$$2Na+S = Na_2S$$
$$Na+X = NaX$$
$$(\text{Where } X = \text{a halogen atom})$$

The excess of sodium left over reacts with water giving NaOH.

The cyanide, sulphide and halide thus formed undergo reactions characteristic to each of them (with the added reagents) under the experimental conditions stated.

(*i*) NaCN on boiling with ferrous hydroxide (obtained from ferrous sulphate and caustic soda) gives sodium ferrocyanide, which in acid medium reacts with ferric chloride yielding a deep-blue colour or precipitate.

$$6NaCN + Fe(OH)_2 = Na_4Fe(CN)_6 + 2NaOH$$

$$4FeCl_3 + 3Na_4Fe(CN)_6 = \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

(*ii*) Na_2S (obtained from the reaction between metallic sodium and sulphur of organic compound) reacts with sodium nitroprusside in alkaline medium yielding a transient violet colour.

$$\underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} + Na_2S = Na_4[Fe(CN)_5NOS]$$

Note that a *blood-red colour* instead of prussian blue may sometimes be observed in the test for nitrogen. This is due to formation of thiocyanate, which *indicates* the presence of both **nitrogen** and **sulphur** in the organic sample.

(*iii*) Sodium halide on reaction with silver nitrate in presence of HNO_3 gives the characteristic ppt. of silver halide.

$$NaX + AgNO_3 = AgX + NaNO_3$$

(Where X= a halogen atom)

3. If either nitrogen or sulphur (or both) be present boiling of sodium extract with an excess of dil. HNO_3 is essential in order to drive away HCN or H_2S (or both) as the case may be.

4. **Additional tests :** Detection of chlorine in presence of bromine and iodine.

(*a*) Wash the ppt. obtained on adding $AgNO_3$ solution with small quantities of water at a time (till a drop or two of the washings give no longer any red ppt. with K_2CrO_4 soln. taken in a test-tube). Now treat the ppt. with 4N $(NH_4)_2CO_3$ solution by shaking and then filter. Add a little of KBr solution to this filtrate—a *pale yellow* ppt. *indicates* **chlorine.**

(*b*) A simpler method than above is: Shake up the precipitated silver halides with 4N $(NH_4)_2CO_3$, filter and acidify the filtrate with dil. HNO_3—a *curdy-white* ppt. *indicates* **chlorine.**

(*c*) Reagents: 100 c.c. of aqueous saturated solution of aniline + 20 c.c. of aqueous saturated solution of toluidine+20 c.c. glacial acetic acid.

Boil in a test-tube a portion of the filtrate (obtained from sodium fusion) with PbO_2 and 2N acetic acid, when bromide and iodide, if any, break up and Br_2 and I_2 go out. Heat the residual solution from this operation with solid $KMnO_4$ and (4N) H_2SO_4 in a test-tube. A drop of the reagent held at the mouth turns **violet** *indicating* the presence of chloride and hence **chlorine** in the original sample.

N.B. Bromine gives a white bromo derivative, while iodine does not react.

5. If the original sample be a liquid, to 1 cm. layer of alkali zinc mixture in a tube add a few drops of the liquid and then cover it up with a further quantity of the reagent, which extends to within about 1¼ cm. of the mouth of the tube and proceed as usual.

6. This test is very sensitive. Several substances containing no halogen may also impart green colour to the flame. So the test is not a confirmatory one. However, that the halogens are absent may be said with a certain amount of certainty, if the flame is not coloured green.

CHAPTER III

DETECTION OF FUNCTIONAL GROUPS

When the sample does not contain nitrogen, follow the procedure (A) and when the sample contains nitrogen, follow the procedure (B) in order to detect the functional groups in the compound.

A. Compounds containing no nitrogen:

In such a case the compound may contain one or more of the following groups: -OH (phenolic or alcoholic); $>C=O$ (carbonyl, —aldehydic and ketonic); —COOH (carboxyl) and —$COOC_2H_5$ (ethyl ester or carbethoxy group). Perform the tests in the order given below :

Experiments	Observations	Inferences
(*a*) Note the colour and odour[1] of the sample.	...	...
(*b*) Burn a portion of the sample on a nickel spatula (or, on a porcelain crucible).	Sooty flame	Aromatic compounds.
(*c*) Shake a portion of the substance with a little water in a test-tube and test the resulting suspension or solution with litmus paper.	(*i*) Acidic towards litmus.	(*i*) Acids and acidic substances such as some phenols, easily hydrolysable esters.
	(*ii*) Neutral to litmus.	(*ii*) Alcohols, carbonyl compounds, esters.
(*d*) Shake a little of the substance with dil. solution of NaOH (5-10%) in a test-tube and warm.	The substance dissolves.	May be phenols and carboxylic acids.

Experiments	Observations	Inferences
(*e*) Shake a portion of the substance with a little water; add a drop of neutral $FeCl_3$ solution to the resulting solution or suspension and note *immediately*[2] the change that might have taken place.	(*i*) Violet, blue or green coloration (permanent or transient).	Phenolic compounds (phenolic —OH gr.).
	(*ii*) Reddish coloration or precipitate.	Some carboxylic acids.
(*f*) Repeat the above expt. by adding a drop of neutral $FeCl_3$ solution to an alcoholic solution of the substance.	Violet, blue or green coloration (permanent or transient).	Phenolic compounds (phenolic —OH gr.).
N.B. *See also* the 'additional tests' given towards the end of this chapter for detection of phenolic compounds.		
(*g*) Sprinkle solid $NaHCO_3$ on aqueous solution of the sample. But if the sample be insoluble in water, sprinkle the solid sample on $NaHCO_3$ solution.	Effervescence[3]	Carboxylic acids (−COOH gr.)
(*h*) Add a little (0·05—0·1 gm.) of the sample to be tested to about 3 c.c. of a saturated solution of 2 : 4 dinitrophenylhydrazine in HCl. Shake, and if no precipitate appears immediately, gently heat to boiling and continue heating the mixture for 2-3 minutes by immersing in a bath of boiling water. Allow it to stand for five minutes. Should no ppt. appear, add water dropwise and scratch inside of the tube till turbid, warm till turbidity disappears, cool and allow to stand.	Yellow, orange or a red ppt.	Carbonyl[4] compounds $>$CO gr. (aldehydic and/or ketonic groups).

Experiments	Observations	Inferences
[If no characteristic ppt. appears even then, dissolve a little of the sample in minimum volume of alcohol by heating just to boiling. Add a portion of this solution to about 3 c.c. of a saturated alcoholic solution of 2 : 4-dinitrophenylhydrazine and proceed as before.] N.B. Sometimes simply mixing of the sample with the solution of 2 : 4-dinitrophenylhydrazine by shaking may lead to the formation of above coloured ppt.		
(*i*) Take in a test-tube equal amounts of semicarbazide hydrochloride and sodium acetate. Dissolve it in minimum quantity of water by heating. Now add a little of the original sample and shake. If the mixture is turbid, add alcohol until a clear solution is obtained and shake. If no ppt. comes down, warm it on water-bath for a few minutes and then cool.	A crystalline ppt.	Carbonyl[5] compounds $>$CO gr. (aldehydic and/or ketonic groups).
Distinction between an aldehyde and a ketone: If a carbonyl group in a compound be detected, then it may be either an aldehyde or a ketone, *i.e.*, the carbonyl group may be present either as an aldehydic gr. (–CHO) or as a ketonic group $\left({}^{R}_{R}\!\!>\!C=O\right)$ Differentiation between the two may be made by performing the following tests:		

Experiments	Observations	Inferences
(*i*) **With Schiff's reagent:** To 2 or 3 c.c. of Schiff's reagent add a little of the original sample. Shake well and allow to stand for two minutes. **N.B.** Don't heat the mixture Development of pink colour is slow in the case of aromatic aldehydes. Besides, a number of aromatic aldehydes, vanillin for example, do not respond to this test at all. Some ketones though respond to this test, the reaction is very very slow. Note that Schiff's reagent is magenta solution, which is rendered colourless by sulphur dioxide.	Development of pink colour.	aldehyde.
(*ii*) **Tollen's reagent:** Mix 1 c.c. each of $AgNO_3$ solution and NaOH solution. Now add NH_4OH dropwise with shaking till a clear solution is *just* obtained. This solution is known as Tollen's reagent. Add a little of the substance under examination to Tollen's reagent. Shake and warm by placing the test-tube in a beaker of boiling water.	Formation of a mirror of *silver* or a *grey* or a *brown* ppt.	aldehyde. [$R\text{-}CHO + Ag_2O = R\text{-}COOH + 2Ag$.]
(*iii*) **Fehling's solution:** Mix equal volumes of Fehling's solution no. 1, and no. 2. Add a little of the substance under investigation to the mixed solution taken in a test-tube and then warm.	A red ppt. of Cu_2O	aldehyde. Cu|O [$R\text{-}CHO + CuO = R\text{-}COOH + Cu_2O$.]
If the above tests for an aldehyde be negative, then the carbonyl compound is a ketone (*i.e.*, it contains a ketonic group).		

Experiments	Observations	Inferences
N.B. Note that aromatic aldehydes do not reduce alkaline copper salt. Of course, Fehling's and ammonical silver nitrate are readily reduced by α-hydroxyketones, i.e., having the grouping —CH(OH)CO-.		
(j) Take about lg. of the sample in a dry test-tube, add a mixture of 4 c.c. acetic anhydride and two drops of conc. H_2SO_4. Warm on water-bath and then pour the contents into about 15 to 20 c.c. of water in a beaker. Stir well.	A ppt. or formation of a separate liquid layer (having a pleasant smell), which floats on water.	Alcoholic or phenolic compounds (—OH group).
(*k*) **Ferric hydroxamate test:** Take a very small portion of the sample in a test-tube; add 2-3 drops of a saturated solution of hydroxylamine hydrochloride in methyl alcohol. Now add in drops a saturated solution of KOH in methyl alcohol till the mixture is alkaline to litmus and heat over a very small flame *just* to boiling. Cool and acidify with normal HCl and add a drop or two of 1% solution of $FeCl_3$.	A violet, red or a pink colour.	Ester[6] (—COOR).
(*l*) **Hydrolysis and distillation:** Take about 1-2g. of the substance in a 100 c.c. flask and add 25 c.c. of (5N) NaOH. Reflux the mixture until the ester layer disappears. Cool and add 10 c.c. of water through the condenser. Now distil the alkaline		

Experiments	Observations	Inferences
mixture and collect about 10 c.c. of the distillate in a test-tube. With the distillate perform the Iodoform test:		
To a little of this distillate in a test tube add a solution of iodine in potassium iodide till a dark-brown colour develops. Warm a little and add a dilute soln. of NaOH drop by drop till the mixture is almost colourless. Now cool the tube under a tap.	A characteristic odour of iodoform without or with a yellow[7] ppt., depending upon the amount of alcohol present in the distillate.	Ethyl ester ($-COOC_2H_5$ group).
(*m*) **Xanthate test:** Take in a clean and dry test tube a little of the original sample and finely powdered KOH approximately in the ratio of 1 : 10 by weight; warm a little. Now cool and add 5-6 drops of ether and 3-4 drops of CS_2. Shake the mixture (*i*) for about 5 minutes; (*ii*) now add 3-4 drops of 1% ammonium molybdate solution, shake very gently and acidify with (2N) H_2SO_4. Add about 10 drops of chloroform and shake.	(*i*) A yellow ppt. (*ii*) The chlorofrom layer becomes violet or reddish-blue.	Alcohol[8] (Alcoholic —OH gr.) Alcohol[8] (Alcoholic —OH gr.).

B. Compounds containing nitrogen:

In such a case the compound under examination may contain one or more of the following groups: $-NO_2$, $-NH_2$, $-CONH_2$. Perform the following experiments in the order given below for detecting the group or groups present:

Experiments	Observations	Inferences
(*a*) Note the colour[1] and odour of the sample		
(*b*) Shake a little of the sample with water in a test-tube and test the resulting solution or suspension with litmus paper.	Acidic Neutral Alkaline	Amine salts[9] Many aromatic amino compounds, Amides Amines (aliphatic and some aromatic).
(*c*) Shake a little of the sample with dil. HCl in a test-tube.	Substance originally slightly soluble or insoluble in water but dissolves in dil. HCl.	Basic substances (*e.g.*, Amines).
(*d*) To a portion of the sample in a test-tube, add conc. solution of NaOH. Observe the effect first when cold, and then on heating.	(*i*) Separation of oily layer. (*ii*) Ammoniacal fishy odour. (*iii*) Ammoniacal[9a] odour;—turning mercurous nitrate paper black; and forming dense white fumes when a glass rod moistened with HCl is held at the mouth of the test tube.	(*i*) Amine salts (*ii*) Salts of lower aliphatic amines. (*iii*) Amides*, Ammonium salts of organic acids.

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* In absence of ammonium salt this stands as a sufficient proof for the amido group. Besides, in case of an amide ammonia is evolved only on heating. However, as ammonia may escape unnoticed, it is advisable to use a comparatively large quantity of the sample in the expt.

Experiments	Observations	Inferences
	(*iv*) The original substance is usually yellow, orange or red and the solution becomes intensely yellow, orange or red coloured.	(*iv*) May be nitro compounds (—NO_2 gr.)
(*e*) **Carbylamine reaction:** Dissolve 3 rice grain of solid NaOH in 2 c.c. alcohol taken in a test-tube. Now add a little of the original sample, two or three drops of chloroform and warm gently.	A characteristic obnoxious[10] odour.	Aliphatic or Aromatic amino compds. (—NH_2 gr.).
(*f*) **Diazo reaction and coupling:** Dissolve a little of the sample in dil HCl, cool and add in portions a cold aqueous solution of sodium nitrite. Cool the solution again and pour a little of it into an *excess* of cold alkaline solution of β-naphthol.	An immediate brilliant scarlet red precipitate or coloration[11].	Aromatic amino compound (Aromatic--NH_2 group)
(*g*) **Mulliken and Barker's tests:** Dissolve a little of the substance in 3 c.c. 50% alcohol. Now add a little solid NH_4Cl (or 5 to 6 drops of 10% $CaCl_2$ solution) and a pinch of Zn-dust. Heat till a vigorous reaction starts. Allow to stand for about five minutes and then filter into ammoniacal $AgNO_3$ (10%) solution in a test-tube.	A black or grey ppt.[12]	Aliphatic or Aromatic nitro compounds (—NO_2 group).

Experimemts	Observations	Inferences
(*h*) In case the $-NH_2$ gr. is absent (as found by expts. *e.* & *f*; described in page 124), take a little of the sample in a test-tube, add 1 c.c. of conc. HCl and a few pieces of metallic tin. Boil for a minute or two, cool under tap. Decant the supernatant liquid. Divide the liquid in *two* portions:		
(*i*) To a little of one portion add about 2 c.c. of strong alcoholic KOH, 2-3 drops of chloroform and then warm.	(*i*) A characteristic obnoxious odour.	$-NO_2$ group (Aliphatic or Aromatic).
(*ii*) To another portion add in portions an aqueous solution of sodium nitrite. Cool again and add a little of this solution to an *excess* of cold alkaline β-naphthol in a test-tube.	(*ii*) A brilliant scarlet-red ppt. or coloration.	Aromatic nitro-compds. (Aromatic $-NO_2$ group).

N.B. It may so happen that in nitrogenous compounds nigrogen containing functional groups, *i.e.*, $-NO_2$, $-NH_2$ and $-CONH_2$ may not be present. Hence if nitrogen be detected in the sample, follow the procedure **(B)** first and if no positive result is obtained thereby, then follow the procedure **(A)** for detecting the functional groups. And, in fact, in every case, to be more systematic, the compounds containing nitrogen (whether the $-NO_2$, $-NH_2$ and/or $-CONH_2$ groups are present or not) should always be examined by following the procedure **(A)** in order to show the presence or absence of groups other than $-NO_2$, $-NH_2$ and $-CONH_2$.

SOME ADDITIONAL TESTS FOR DETECTION OF FUNCTIONAL GROUPS

A. Phenolic—OH gr. :

(*i*) **Back dye tests:** Take one or two drops of aniline in a test-tube and dissolve it in dil. HCl. Cool under tap. Add a dilute aqueous solution of sodium nitrite in portions. Cool again. Add a few drops of this diazotised solution to an *excess* of **alkaline** solution of the sample—an immediate brilliant scarlet-red ppt. or coloration *indicates* the presence of a phenolic —OH group.

(*ii*) **Liebermann's reactions :** Take in a dry test-tube about 0·5 g. of the original sample. Now add to it a trace of solid $NaNO_2$ and 1. c.c. of conc. H_2SO_4. Warm the mixture gently, **a green or blue colour** is developed. Pour this solution into water, when the colour changes to **red**. Now add excess of caustic soda, when the colour again changes to green or blue.

(*iii*) **Phthalein tests :** Take a little of the substance and about half its bulk of phthalic anhydride in a dry test-tube. Add one or two drops of conc. H_2SO_4 and heat the mixture. Cool, add a few drops of water and dil. NaOH solution gradually with shaking till alkaline. Dilute with water (and filter, if necessary). Development of colours, **red** or **yellow-green** fluorescence *indicates* the presence of phenolic —OH gr.

B. —COOH gr : Esterification:

Take a small portion of the sample in a small and dry round-bottomed flask; add about 3 c.c. absolute alcohol and shake. Add 3-4 drops of conc. H_2SO_4. Attach an air condenser and warm for about ten minutes by placing it in a bath of hot water (70°C). Cool and pour down the mixture into a small beaker containing about 20 c.c. water ; —separation of oily layer, which does not dissolve in cold and dilute alkali; but possesses a characteristic fragrant smell *indicates* the presence of **—COOH gr.**

Notes on detection of functional groups

1. *Colour and odour*. The colour and odour of the original sample should always be noted. It may sometimes

help to guess the class to which the substance under examination belongs. As for example, nitro compounds are generally yellow (pale or deep) or orange coloured. Hydrocarbons, alcohols, phenols, aldehydes, ketones and acids are generally colourless. Esters, alcohols and aromatic hydrocarbons may have sweet and pleasant smell. Pungent and irritating odours are given by lower aliphatic acids, acid halides, etc. Phenols, lower aliphatic ketones, etc. possess characteristic smell. It is, however, a matter of practice to identify the type of odour of a substance under investigation.

2. The colour exhibited by *some* phenolic compounds on reaction with ferric chloride solution is very much transitory in nature. Hence the effect should be noted immediately after addition of $FeCl_3$ solution.

3. Not only the compounds containing $-COOH$ gr. give effervescence with $NaHCO_3$ but there are others such as chlorophenols, nitrophenols, amine salts, easily hydrolysable esters give sufficiently strong acid reactions to produce effervescence with $NaHCO_3$.

4. 2 : 4-dinitrophenylhydrazine forms 2 : 4-dinitrophenylhydrazone with carbonyl compounds (*i.e.*, compounds containing $>C=O$ group).

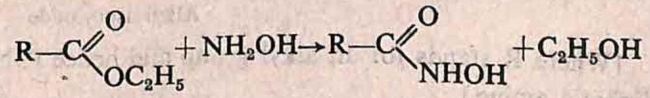
$$>CO+H_2N\text{-}NHC_6H_3(NO_2)_2 \rightarrow \underset{\text{2:4-dinitrophenylhydrazones}}{>C=N\text{-}NH\text{-}C_6H_3(NO_2)_2}+H_2O$$

5. Carbonyl compounds react with semi-carbazide hydrochloride to form crystalline derivatives known as semicarbazones.

$$>CO+H_2N\text{-}NH\text{-}CONH_2 \rightarrow \underset{\text{semicarbazones.}}{>C=N\text{-}NH\text{-}CONH_2}+H_2O.$$

6. **Note that the groups other than the ester, that respond to ferric hydroxamate test are beyond the scope of the pass syllabus.**

Hydroxamic acids are formed by the action of hydroxylamine on esters.



$$R-C\begin{smallmatrix}\nearrow O\\ \searrow OC_2H_5\end{smallmatrix}+NH_2OH\rightarrow R-C\begin{smallmatrix}\nearrow O\\ \searrow NHOH\end{smallmatrix}+C_2H_5OH$$

Hydroxamic acid in slightly acid solution exhibits coloration by forming coloured complex with ferric chloride solution.

Hence, before performing this expt. make sure that the ferric chloride solution does not produce any coloration with the original sample.

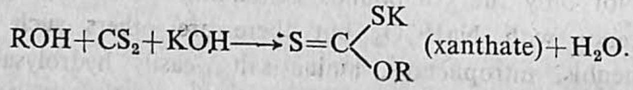
7. The ester is hydrolysed by alkali into alcohol (here ethyl alcohol) and the sodium salt of corresponding acid. On distillation ethyl alcohol collects in the distillate.

$$R\text{-}COOC_2H_5+NaOH=R\text{-}COONa+C_2H_5OH.$$

The presence of ethyl alcohol in the distillate is confirmed by iodoform test. With iodine and caustic alkali, ethyl alcohol forms iodoform.

$$C_2H_5OH+4I_2+6NaOH=CHI_3+HCOONa+5NaI+5H_2O.$$

8. The yellow ppt. is due to xanthate, which is formed, when alkoxide obtained from alcohol and KOH reacts with CS_2.



$$ROH+CS_2+KOH \longrightarrow S=C\begin{cases}SK\\OR\end{cases}\text{(xanthate)}+H_2O.$$

With ammonium molybdate, xanthate in slightly acid solution forms a coloured complex.

9. Besides amine salts, some other compounds such as nitrophenols react acidic towards litmus.

9a. Amides undergo rapid hydrolysis by alkalis and ammonia is evolved:

$$RCONH_2+H_2O \text{——} RCOOH+NH_3$$

10. Both aliphatic and aromatic amines respond to this test. This reaction is also called isocyanide reaction and is represented by the following equations:

$$Ar\text{-}NH_2+CHCl_3+3KOH=\underset{\text{Aryl isocyanide}}{ArNC}+3KCl+3H_2O$$

[Where Ar stands for an aryl group; hence $ArNH_2$ is an aromatic amine.]

Similarly, $R\text{-}NH_2+CHCl_3+3KOH=\underset{\text{Alkyl isocyanide}}{RNC}+3KCl+3H_2O$

[Where R stands for an alkyl group and hence $R\text{-}NH_2$ is an aliphatic amine.]

11. Salts of aromatic primary amino compounds react with nitrous acid ($NaNO_2+HCl$) *in the cold* to produce soluble

diazonium salts. This reaction is called Diazo reaction. [During diazotisation temperature should be kept between 0°C – 5°C and an aqueous solution of sodium nitrite should be added in portions, till the reaction mixture produces a blue colour with KI—starch paper.] The diazonium salt thus produced couples with phenols and other aromatic hydroxy derivatives in **alkaline** medium to give brilliant coloured azo-dyes. With aniline, for example, the reactions is:

$$C_6H_5NH_2HCl + HONO \rightarrow \underset{\text{Diazo-salt}}{C_6H_5N{=}NCl} + 2H_2O$$

$$C_6H_5N{=}NCl + \underset{\beta\text{-naphthol}}{C_{10}H_7OH} \rightarrow \underset{\text{a scarlet azo-dye}}{C_6H_5N{=}NC_{10}H_6OH} + HCl.$$

12. The nitro-compounds are reduced by zinc dust and NH_4Cl (or $CaCl_2$) to hydroxylamine derivatives, which reduce alkaline silver nitrate into metallic silver.

$$R\text{-}NO_2 \xrightarrow{4H} R\text{-}NHOH + H_2O$$

$$R\text{-}NHOH + Ag_2O \longrightarrow 2Ag + H_2O + RNO.$$

(where R *stands for* an alkyl or aryl radical).

Specimen Records of Analytical Results

Sample No……

Date……

The given sample is a colourless, crystalline solid having a pleasant aroma.

Detection of elements (Nitrogen, sulphur and halogens): The substance was fused with metallic sodium in an ignition tube, which was then immersed, while red hot into 20 c.c. distilled water taken in a mortar and broken by tapping. The mixture was filtered after grinding the fused mass and broken glass pieces. The following expts. were performed taking a small portion of the filtrate at a time.

Experiments	Observations	Inferences
(*i*) To a portion of the filtrate freshly prepared ferrous sulphate solution was added. After boiling the mixture for about a minute it was allowed to cool, acidified with conc. HCl and finally a drop or two of ferric chloride was added.	No blue ppt. or coloration.	Nitrogen absent.
(*ii*) To a portion of the filtrate a drop or two of freshly prepared sodium nitroprusside solution was added.	No violet coloration.	Sulphur absent.
(*ii*) A little of the filtrate was acidified with dil. HNO_3 and $AgNO_3$ solution was added to it.	No ppt.	Chlorine, Bromine, Iodine —absent.

Detection of functional group: As the sample does not contain nitrogen, the question of examining nitrogen containing functional group (or groups) does not arise at all. To detect the functional group the following experiments were performed in succession.

Experiments	Observations	Inferences
(*i*) A portion of the sample was burnt on a porcelain crucible.	Sooty flame	Aromatic compound.
(*ii*) A portion of the sample was shaken with water and the resulting suspension was tested with litmus paper.	The sample did not dissolve and the suspension had no action on litmus paper.	Water ... insoluble neutral substance.
(*iii*) A portion of the sample was shaken with a dilute solution of NaOH and warmed.	The sample dissolved and turned yellow.	Acidic nature
(*iv*) (*a*) A portion of the sample was shaken with a little water and the resulting suspension was treated with a drop of neutral ferric chloride solution.	A violet colour developed.	Phenolic $-OH$ gr.
(*b*) The above expt. was repeated by replacing water by ethanol.	A violet colour developed.	Phenolic $-OH$ gr.
(*v*) To a solution of $NaHCO_3$ in water, the solid sample was sprinkled.	No effervescence.	$-COOH$ gr. absent.
(*vi*) To 3 c.c. of a solution of 2: 4 dinitrophenylhydrazine a portion of the sample mixed with dil HCl was added. The mixture was then shaken for thorough mixing.	An orange red ppt.	$\rangle C=O$ gr.
(*a*) To about 2 c.c. of Schiff's reagent a little of the original sample was added. The mixture was allowed to stand for two minutes after thorough shaking.	No Pink* colour developed	

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* A number of aromatic aldehydes give negative result.

Experiments	Observations	Inferences
(*b*) To about 3 c.c. of Tollen's reagent a little of the substance under investigation was added. After thorough mixing the test tube was warmed by placing it in a beaker of boiling water.	Formation of a mirror of silver.	Aldehyde
(*vii*) A portion of the substance was refluxed with alkali and then distilled. With a little of the distillate iodoform test was performed. (Since a colour developed in ferric chloride test, ferric hydroxamate test was not performed.)	No yellow ppt. and no characteristic odour.	$-COOC_2H_5$ gr. absent.
(*viii*) A portion of the sample was treated with KOH, ether and CS_2; and was shaken for about 5 minutes. Then it was acidified with H_2SO_4 after addition of a few drops of ammon molybdate. Finally, it was shaken with chloroform.	No yellow ppt. and no coloration of chloroform layer.	Alcoholic $-OH$ absent.

Hence nitrogen, halogens and sulphur are absent and the functional groups that the sample contains are : aldehydic ($-CHO$) group and phenolic hydroxyl ($-OH$) group.

Sample No.....

Date......

The given sample is a yellow solid.

Detection of elements (nitrogen, sulphur and halogens): The substance was fused with metallic sodium in an ignition tube, which was then immersed, while red hot into 20 c.c. distilled water taken in a mortar and broken by tapping. The mixture was filtered after grinding the fused mass and broken glass pieces. The following expts, were performed taking a small portion of this filtrate at a time.

Experiments	Observations	Inferences
(*i*) To a portion of the filtrate freshly prepared ferrous sulphate solution was added. After boiling the mixture for about a minute it was allowed to cool, acidified with conc. HCl and finally a drop or two $FeCl_3$ solution was added.	Deep-blue ppt.	Nitrogen present.
(*ii*) To a portion of the filtrate a drop or two of a freshly prepared sodium nitroprusside solution was added.	No violet coloration.	Sulphur absent.
(*iii*) To a little of the filtrate excess of dil.HNO_3 was added and boiled to drive away HCN. It was then cooled and $AgNO_3$ solution was added.	No ppt.	Chlorine, bromine iodine absent.

Detection of functional group : Since the substance contains nitrogen, nitrogen containing functional group or groups may be present. To detect the functional groups the following experiments were performed in succession:

Experiments	Observations	Inferences
(*i*) A little of the sample was shaken with water and the resulting mixture was tested with litmus paper.	The substance did not dissolve and the resulting mixture had no action on litmus paper.	Water insoluble neutral substance.
(*ii*) A small portion of the sample was shaken with lil. HCl.	The substance dissolved.	Basic nature
(*iii*) A small portion of the sample was shaken with conc. solution of NaOH and heated.	The yellow colour deepens.	May be—NO_2 gr.

Experiments	Observations	Inferences
(*iv*) A portion of the sample was warmed with alcoholic NaOH and chloroform.	A chracteristic obnoxious odour.	Aromatic or aliphatic amino compound ($-NH_2$) gr.
(*v*) A portion of the sample was treated with $NaNO_2$ and dil. HCl and a little of this cooled solution was added to an excess of alkaline β-naphthol solution.	An immediate brilliant scarlet red ppt.	Aromatic $-NH_2$ gr.
(*vi*) An aqueous alcoholic solution of a small portion of the sample was treated with zinc dust and NH_4Cl and was finally filtered into ammoniacal $AgNO_3$ solution.	A black ppt.	Aromatic $-NO_2$ gr.
(*vii*) An aqueous suspension of a portion of the sample was treated with a drop of neutral $FeCl_3$.	No characteristic change	Absence of phenolic $-OH$ gr.
(*viii*) The expt.-vii was repeated by substituting water by alcohol.	No characteristic change	Absence of phenolic $-OH$ gr.
(*ix*) Hydrochloric acid solution of the sample was treated with 2 : 4 dinitrophenylhydrazine.	No ppt.	Absence of $>C=O$ gr.
(*x*) A portion of the sample was warmed on water-bath with acetic anhydride and a few drops of conc. H_2SO_4. It was then poured into water and stirred well.	Neither any ppt. nor a separate liquid layer (having a pleasant smell) did appear.	$-OH$ group (phenolic or alcoholic) absent.
(*xi*) A portion of the sample was refluxed with alkali and distilled. With a little of the distillate iodoform test was carried out.	No yellow ppt and no characteristic odour.	$-COOC_2H_5$ gr. absent.

Hence, the sample contains nitrogen and nitrogen containing functional groups $-NO_2$ and $-NH_2$.

2. REACTIONS AND TESTS OF SOME COMMON ORGANIC COMPOUNDS

INTRODUCTION

In this section of the book the principal reactions and tests of some common organic compounds are described. Some of these reactions are employed in subsequent general scheme of qualitative analysis of an unknown organic compound or as principal special tests. Before proceding with the qualitative analysis of unknown sample a student, therefore, must practise these reactions with known substances and should never avoid it.

It should also be noted here that in carrying out some reactions of organic compound a neutral solution of the sample is required. Hence, a portion of the solution of solid* or one-third portion (one third is to be kept reserved) of the liquid (or the given solution) is to be neutralised, if it is not already neutral. If it reacts alkaline, neutralise it with dilute nitric acid by adding the dilute acid dropwise and testing from time to time till a drop of the resulting solution taken on a glass rod just turns blue litmus red. If, however, as a result of addition of acid the resulting solution becomes distinctly acidic, add dilute ammonia dropwise till the smell of ammonia persists and then boil off excess ammonia. If, on the other hand, the solution (or suspension) reacts acidic, neutralise with powdered sodium carbonate by adding a little by little and if the resulting mixture becomes alkaline on addition of carbonate, add in portion a little more of the original sample till the solution reacts neutral. It must, however, be borne in mind that the solution may be left faintly acidic but it never be left alkaline for the purpose of carrying out necessary wet reactions with it. It should further be noted that if the solution be faintly acidic, there is no need of neutralisation; proceed with the solution as such for carrying out necessary reactions.

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*If a solid sample be given shake about one gram of the solid with 10 c.c. water, heat and filter, if necessary. If the solid be insoluble in water, treat the suspension in water with acid or base as may be necessary for neutralisation.

CHAPTER 1

REACTIONS AND TESTS

1. Formic acid, HCOOH

Free acid is a colourless liquid having a pungent smell. It is miscible with water in all proportions. The free acid and its ammonium salt, if heated, completely volatilises away.

Preliminary tests

Experiments	Observations
(*i*) Heat carefully in a clean and dry test-tube	
(*a*) a little of formic acid,	(*a*) The substance completely volatilises away.
(*b*) a little of sodium or potassium formate.	(*b*) A residue is left behind and hydogen gas, which can be set fire to is evolved.
(*ii*) Add conc. H_2SO_4 to a little formic acid or a formate; warm and ignite the issuing gas.	An effervescence occurs in the cold and the issuing gas burns with a pale blue flame.

Wet-tests

Experiments	Observations
(*iii*) Add Denige's reagent to a solution of formate or formic acid and boil.	A white sand like ppt. comes down on boiling.
(*iv*) To a neutral solution of formate add freshly prepared neutral* ferric chloride. Divide the coloured solution into *two* parts:	A red colour develops.
(*a*) To one portion add dil HCl.	(*a*) Colour is discharged.

---

*To a little of ferric chloride solution add NH_4OH or NaOH solution till a permanent ppt. just appears. Filter, the resulting filtrate is termed *neutral ferric chloride* and use it for the above reaction.

Experiments	Observations
(*b*) Boil the other portion.	(*b*) A brown ppt. appears.
(*v*) To a little of dilute solution of formic acid or a formate add silver nitrate solution.	A white ppt. in the cold, which slowly turns black[1] on standing. This transformation is facilitated on warming.
(*vi*) Warm a solution of formic acid or a formate with mercuric chloride solution.	A white ppt. or a grey metallic deposit with excess of formic acid or a formate.

2. Acetic acid, CH_3COOH

A colourless liquid, having a characteristic vinegar odour, miscible with water in all proportions. *Free acid or its ammonium salt, if heated completely volatilises off.* But with calcium salt an inflammable vapour is given off and a residue is left behind.

Preliminary tests

Experiments	Observations
(*i*) Warm an acetate with dilute or conc. H_2SO_4.	Vinegar like smell is evolved.
(*ii*) *Cacodyl oxide test*: Mix equal parts of a dry acetate and arsenious oxide (both being taken in small quantity) in a test-tube and finally heat.	
Hold your thumb at the mouth of the test-tube and inhale the thumb.	An extremely nauseating odour[2].

---

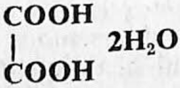
[1] Ammonia prevents the reduction of silver nitrate.

[2] Don't inhale *directly*, as the evolved vapour is *highly poisonous*. Discard the test-tube as soon as the test is over.

Wet-tests

Experiments	Observations
(*iii*) Add to a cold solution of acetic acid or an acetate a little of Denige's reagent and boil.	No ppt. either in the cold or from hot solution.
Now add a drop or two of a two per cent solution of $KMnO_4$.	Permanganate is not decolourised.
(*iv*) Test with $FeCl_3$ solution as indicated under formic acid.	Same as in the case of formic acid.
(*v*) Add $AgNO_3$ solution to a conc. neutral solution of acetate and boil.	A white ppt., which does not turn black on boiling (*see* the test under formic acid).
(*vi*) Add mercuric chloride solution to a solution of the acid or an acetate.	No ppt.* (A distinction from formic acid).

3. Oxalic acid



$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \; 2H_2O$$

A colourless solid, soluble in water, crystallises with two molecules of water of crystallisation.

---

*A ppt. is, however, obtained with ammonium acetate but no black or grey ppt. comes down.

Preliminary tests

Experiments	Observations
(*i*) Heat cautiously over a small flame oxalic acid crystals taken in a clean and dry test-tube.	Dissolves in its own water of crystallisation, no charring occurs, volatilises off completely, yielding a feather-like sublimate[1].
(*ii*) Warm the acid or its salt with conc. H_2SO_4 and allow the issuing gas to pass through lime water.	Lime water turns milky.

Wet-tests

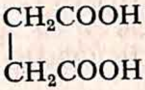
Experiments	Observations
(*iii*) Add $CaCl_2$ solution to a neutral solution of an oxalate.	A white ppt.
Divide the ppt. into *two* parts: To one portion add dil. HAc.	Ppt. does not dissolve.
To the other portion add dil. HCl or dil. HNO_3.	Ppt. dissolves
(*iv*) To a neutral solution of an oxalate add $AgNO_3$ solution	A white crystalline ppt.
Divide the ppt. into *two* parts:	
To one portion add dil. NH_4OH To the other portion add dil. HNO_3.	The ppt. dissolves in both the reagents.

---

[1] On strong heating oxalic acid first decomposes into carbon dioxide and formic acid, the latter subsequently decomposes into carbon monoxide and water, both of which escape.

Experiments	Observations
(*v*) Add a little dil. H_2SO_4 to a solution of oxalic acid or to a neutral solution of an oxalate. Warm just to boil, add $KMnO_4$ solution in drops.	The colour of permanganate is discharaged.
(*vi*) To a solution of oxalic acid or oxalate add Denige's reagent and then boil.	A white ppt. in the cold, which does not dissolve on boiling.

4. Succinic acid.



$$\begin{array}{l} CH_2COOH \\ \vert \\ CH_2COOH \end{array}$$

A colourless, crystalline solid, soluble in hot water.

Preliminary tests

Experiments	Observations
(*i*) Heat a little of the solid in a clean and dry test-tube.	A sublimate is formed and irritating fumes are given off.
(*ii*) Warm a few crystals of the acid with conc. H_2SO_4.	The acid dissolves and no charring[1] occurs.

Wet-tests

Experiments	Observations
(*iii*) *Fluorescein test*: Take a small quantity of the solid and mix with twice its weight of resorcinol. Add a few drops of conc. H_2SO_4 to the mixture and (*a*) heat gently.	(*a*) A deep-red solution is obtained on heating.

---

[1] Slight charring occurs, if strongly heated.

Experiments	Observations
(*b*) Pour the contents of the test-tube into a large volume of water; and	(*b*) Deep-red solution changes to an orange-yellow solution, which exhibits an intense[1] green fluorescence.
(*c*) then add NaOH solution.	(*c*) Fluorescence is intensified and the solution changes to bright red.
(*iv*) To a neutral solution of the sample add a drop or two of freshly prepared neutral ferric chloride solution.	Buff-coloured ppt. disappearing on addition of dil. HCl.
(*v*) To a portion of the neutral solution add an equal volume of $CaCl_2$ solution, shake well, scratch and boil.	A white ppt. soluble in acetic acid.
(*vi*) Add $AgNO_3$ solution to a portion of the neutral solution of the sample and finally add dil. NH_4OH.	A white ppt. appears. The ppt. dissolves in dil. NH_4OH.

5. Tartaric acid.

$$\begin{array}{l}\mathrm{CH(OH)COOH}\\ \mathrm{CH(OH)COOH}\end{array}$$

A colourless, crystalline solid, soluble in water. It exists in four stereo-isomeric forms of which dextro variety is the most common.

Preliminary tests

Experiments	Observations
(*i*) Heat the acid or tartrate in a clean and dry test-tube.	The substance chars.
(*ii*) Warm the solid with conc. H_2SO_4	The substance readily chars.

---

[1] Note that a feeble fluorescence is also observed, when simply resorcinol and conc. H_2SO_4 are heated together. Moreover, besides succinic acid other polybasic acids such as citric, tartaric, etc. may sometimes exhibit feeble fluorescence. Hence, a slight or feeble fluorescence is no confirmation for a succinate or succinic acid.

Wet-tests

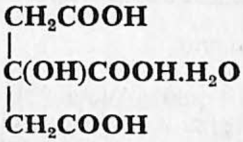
Experiments	Observations
(*iii*) To a portion of the neutral and concentrated solution add an excess of $CaCl_2$ solution, shake and scratch inside of the test-tube.	A white crystalline ppt. soluble in hot dilute acetic acid.
(*iv*) *Mirror test*: Clean a test-tube first with caustic soda and then with dil. HNO_3 and finally wash with distilled water. Take a little of the neutral solution of the sample in the test-tube thus cleansed. (*a*) Add $AgNO_3$ solution to it, (*b*) and continue addition till the precipitation is complete. Now add dil. NH_4OH dropwise and with constant shaking till the ppt. almost and not completely redissolves (the contents of the test-tube should look slightly turbid at this stage). Warm the test-tube placing it in a beaker of boiling water for a few minutes.	(*a*) A white crystalline ppt. appears. (*b*) The walls of the test-tube get coated with shining mirror of silver.
(*v*) *Denige's modification of Mohler's test*: Take 2 c.c. conc. H_2SO_4, and 2-3 drops of a 2% solution[1] of resorcinol, then two drops of the neutral solution of the sample, and finally warm.	A reddish-violet coloration.
(*vi*) *Fenton's test*[2]: To about 5-6 c.c. of a dilute solution of tartaric acid or tartrate add just one or two drops of a freshly prepared, saturated solution of ferrous sulphate. Now add a drop of a dil. solution of hydrogen peroxide to the above mixture and then immediately add an excess of NaOH solution.	A deep violet coloration.

---

[1] 0·5g. resorcinol in 25 c.c. of 1% H_2SO_4.

[2] Excess of both ferrous sulphate and H_2O_2 is to be *always* avoided.

6. Citric acid



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH.H_2O \\ | \\ CH_2COOH \end{array}$$

A colourless solid, soluble in water, crystallises with one molecule of water.

Preliminary tests

Experiments	Observations
(*i*) Heat in a clean and dry test-tube citric acid or a citrate.	The substance chars and acrid smelling fumes are given off.
(*ii*) Warm *gently* citric acid or a citrate with a little of conc. H_2SO_4 in a test-tube.	Slow[1] charring occurs.

West-tests

Experiments	Observations
(*iii*) To a portion of the neutral solution add an equal volume of calcium chloride solution. Shake, scratch and finally boil.	No. ppt. even on shaking and scratching but on boiling[2] only.
(*iv*) Add cadmium chloride solution to a portion of the neutral solution taken in a test-tube.	A white gelatinous ppt. insoluble in hot water but readily soluble in hot acetic acid.
(*v*) *Silver nitrate test*: See 'Mirror test' indicated under tartaric acid	A curdy-white ppt. soluble in ammonia is obtained, but no reduction takes place on boiling for a short[3] time.

---

[1] Note that tartrate or tartaric acid chars immediately.

[2] A distinction from tartaric and oxalic acids, which give ppt. in the cold.

[3] Prolonged boiling, however, results in a slight reduction but no fine mirror like that produced by a tartrate is obtained.

Experiments	Observations
(*vi*) Add an equal volume of Denige's reagent to a little portion of the solution of the acid or of a citrate; boil and then add a drop or two of a 2% solution of $KMnO_4$.	The colour of permanganate is discharged and a white ppt. or turbidity appears.

7. Benzoic acid. C_6H_5COOH

The acid is a colourless, plate-like or a needle-shaped crystalline solid, sparingly soluble in cold water but more soluble in hot water.

Preliminary tests

Experiments	Observations
(*i*) Heat a little of the acid in a clean and dry test-tube.	The acid first sublimes and then melts. Copious white fumes, which excite sneezing and/or coughing are given off.
(*ii*) Warm the solid acid with a little conc. H_2SO_4.	The solid dissolves in conc. acid but no charring occurs.
(*iii*) Mix the solid (free acid or benzoate) with four times of dry sodalime and heat in a test-tube.	
(*a*) Take the smell, and	(*a*) Characteristic smell of benzene.
(*b*) ignite the issuing gas.	(*b*) The evolved gas burns with a sooty flame.

Wet-tests

Experiments	Observations
(*iv*) To a portion of the neutral solution add dilute mineral acid, shake and scratch.	A white crystalline ppt. dissolves on boiling but reappears on cooling.

Experiments	Observations
(*v*) To a portion of the neutral solution add Denige's reagent.	Same observation as in expt. -(*iv*) above.
(*vi*) To a portion of the neutral solution add a drop or two of a freshly prepared neutral $FeCl_3$ solution.	A buff-coloured ppt.
Add dil. HCl to the above ppt.	Buff-coloured ppt. disappears but a white crystalline ppt. reappears.
(*vii*) Take about 0.1g. of a benzoate or the free acid in a clean and dry test-tube, add about 2 c.c. of alcohol and *shake well.* Now add a few drops of conc. H_2SO_4 and warm the test-tube for a few minutes in a bath of boiling water. Cool and pour the contents of the, test-tube into a basin containing a little of sodium carbonate solution.	Fruity smell

8. Salicylic acid, $C_6H_4(OH)COOH$

The acid is a colourless, odourless, crystalline solid. It is very sparingly soluble in cold water but dissolves readily in hot water.

Preliminary tests

Experiments	Observations
(*i*) Heat	
(*a*) gently in a dry test-tube a little of the acid,	Acid melts at first and then sublimes.
(*b*) rapidly.	Characteristic odour of phenol is given off.
(*ii*) Warm a little of the acid (or a salicylate) with conc. H_2SO_4.	The solid dissolves, the resulting solution darkens and gases are evolved.

Experiments	Observations
(*iii*) Make an intimate mixture of the acid (or salicylate) and sodalime and then heat the mixture strongly.	Characteristic odour of phenol is evolved.
(*iv*) *Oil of wintergreen test*: Take about 0.1g. of the solid acid (or a salicylate) in a test-tube, add about 1 c.c. of a mixture of MeOH and conc. H_2SO_4 containing about 0·3 c.c. of the acid. Heat gently for about 3-4 minutes.	A characteristic fragrant odour. [The odour becomes more pronounced on cooling the test-tube and pouring its contents into a little solution of sodium carbonate kept in a shallow vessel say a basin; *cf.* benzoic acid.]

Wet-tests

Experiments	Observations
(*v*) To a portion of the neutral solution add dil. mineral acid.	A white crystalline ppt., which dissolves on boiling but reappears on cooling.
(*vi*) Add an excess of bromine water to a portion of the neutral solution.	A pale-yellow crystalline ppt. comes down.
(*vii*) Test with Denige's reagent (*see* benzoic acid).	Same as in the case of benzoic acid.
(*viii*) To a portion of the neutral solution add a drop or two of a freshly prepared neutral ferric chloride solution.	An intense violet colour develops.
Divide the coloured solution into *two* parts:	
(*a*) To one part add dil. HCl.	(*a*) colour is discharged;
(*b*) To the other add a moderate quantity of acetic acid.	(*b*) colour is not[1] discharged.
(*ix*) Try *Phthalein test* (cf. page 126).	

---

[1] A distinction from phenol, the colour given by phenol with ferric chloride is discharged by acetic acid.

9. Phenol, C_6H OH

It is a colourless, crystalline, low melting solid[1]. It has a characteristic carbolic smell. It is not much soluble in water. But it dissolves readily in alkali. It cannot liberate carbon dioxide from carbonate or bicarbonate.

Preliminary tests

Experiments	Observations
(*i*) Heat a few crystals (or drops) of the sample in a dry test-tube.	The substance volatilises[2] off completely, a characteristic phenolic odour is given off.
(*ii*) Warm a few crystals (or drops) with conc. H_2SO_4.	No charring occurs.
(*iii*) *Liebermann's reaction*: Add a small crystal of sodium nitrite to a little of the solid (or a drop of the liquid) taken in a test-tube. Warm the mixture, cool and	
(*a*) then add about 1 c.c. of conc. H_2SO_4;	(*a*) Blue or green colour develops.
(*b*) pour the mixture into an excess of water in a beaker;	(*b*) Blue or green colour changes to red.
(*c*) now add caustic soda till the solution becomes alkaline.	(*c*) The solution turns blue or green again.

Wet-tests

Experiments	Observations
(*iv*) Add bromine water to an aqueous solution of phenol till the precipitation is complete.	A yellowish-white ppt. comes down.
(*v*) To an aqueous solution of phenol add a drop or two of a freshly prepared neutral ferric chloride solution.	A violet colour develops.
Divide the coloured solution into *two* parts:	

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[1] On exposure to air the solid melts to a red or pinkish syrupy liquid and that is why it is sometimes found to be in this state in our laboratories.

[2] The solid first melts and then volatilises away.

Experiments	Observations
To one part add dil. HCl and to the other add acetic acid. (*vi*) Try *Phthalein test* (cf. page 126).	Colour is discharged[1]

10. **Resorcinol** (m-dihydroxy benzene)

m-$C_6H_4(OH)_2$

It is a colourless (when pure) and odourless solid, freely soluble in water.

Experiments	Observations
1. To an aqueous solution of resorcinol add a drop or two of freshly prepared neutral ferric chloride solution.	A bluish violet colouration develops.
2. To 1c.c. of the aqueous solution add 1 c.c. of Fehling's* solution and subsequently warm the mixture.	A red ppt. of Cu_2O slowly comes down.
3. Try Phthalein test (cf. page 126)	A yellow-green fluorescence
4. Try Fluorescein test (cf. Page 140-141).	See Succinic acid

11. Betanaphthol, $C_{10}H_7OH$

It is a crystalline solid. It crystallises in leaflets. It possesses a faint phenolic odour. It is insoluble in water but soluble in alkali.

Preliminary tests

Experiments	Observations
(*i*) Heat a little of the solid in a clean and dry test-tube.	No characteristic change, but the substance melts down to a liquid.
(*ii*) Warm a little of the solid with conc. H_2SO_4.	A blackish green colour develops.

---

[1] A distinction from salicylic acid (*see* salicylic acid, p. 146).

*It will also reduce siliver nitrate solution on warming.

Wet-tests

Experiments	Observations
(*iii*) To a little of the solution of the sample in alcohol add a drop of freshly prepared neutral $FeCl_3$ solution and note immediately the change of colour.	A green coloration and afterwards a flocculant ppt.
(*iv*) Dissolve a little of the substance in conc. caustic potash, add a drop of chloroform and finally warm.	A blue colour develops.
(*v*) To a suspension of betanaphthol in water add sodium hypobromite solution and shake	A yellow colour develops.
(*vi*) *Back-dye test*: Dissolve a little of aniline in dil. HCl. Cool under tap and add a dil. solution of sodium nitrite in portion until a drop of the solution turns starch iodide paper blue. Cool again and add a little of this solution to an excess of a solution of Betanaphthol in caustic soda.	A brilliant scarlet red coloration or ppt. appears.
(*vii*) Try *Phthalein test* (cf. page 126).	

12. Methyl alcohol, CH_3OH

Methyl alcohol is a colourless, neutral, volatile and inflammable liquid having a pungent smell. (Faint alcoholic odour is also noticeable.) It is miscible with water in all proportions.

Preliminary tests

Experiments	Observations
(*i*) Heat in a dry test-tube a few drops of the liquid.	Inflammable vapours are given off and the liquid completely volatilises away.
(*ii*) Try *oil of wintergreen test* as indicated under salicylic acid.	Same as with salicylic acid.

Wet-tests

Oxidation of methyl alcohol to formaldehyde: Take an aqueous solution of alcohol in a test-tube. Keep the test-tube in cold water contained in a beaker. Heat a clean copper spiral in the non-luminous Bunsen flame. Plunge the spiral, when red-hot into this alcohol. Repeat alternate heating and plunging of the spiral into the aqueous solution several times and replace the water of the beaker from time to time by fresh cold water. The liquid in the tube contains solution of formaldehyde and unconverted methyl alcohol. Carry out the following reactions taking a small portion of the liquid each time.

Experiments	Observations
(*iii*) To 5 c.c. of the Schiff's reagent add a few drops of the oxidised solution.	Development of pink colour, which deepens gradually.
(*iv*) *Rimini's test*: Add 1c.c. each of a freshly prepared one per cent aqueous solution of phenylhydrazine hydrochloride and 0.5% aqueous solution of sodium nitroprusside to a 5 c.c. portion of the oxidised liquid. Finally, add caustic soda solution in excess.	Development of intense indigo blue colour.
(*v*) *Resorcinol test*: Hold a test-tube containing 2-3 c.c. of conc. H_2SO_4 in an inclined position. In another test-tube take 1 c.c. of the oxidised liquid and a drop of 0·5% resorcinol. Now add this mixture to the above acid (conc. H_2SO_4) carefully down the side of the test-tube.	A reddish-violet ring appears at first at the junction of liquid layers. With the passage of time a white ppt. changing to reddish-violet appears in the aqueous layer above the ring.

Oxidation of methyl alcohol to formic acid: Take about 10 c.c. of a 50% solution of well-cooled sulphuric acid (prepared by mixing 1 vol. of conc. acid with 1 vol. of water) and add 5 c.c. of methyl alcohol to it. Add this mixture of alcohol and acid to a 5 c.c. of a saturated solution of $K_2Cr_2O_7$ taken in a 50 c.c. distilling flask fitted with a long delivery tube, the end of which is kept immersed under distilled water in a test-tube. Hold this test-tube in a small beaker full of water. Take out a drop or two of this green solution for carrying out *Morphine test* indicated below. Allow the rest to stand for about five minutes and then distil. Neutralise the distillate with a dilute solution of sodium carbonate, boil to drive away formaldehyde, if there be any. Perform the tests and observe the changes as indicated under formic acid (pages 136-37) with the following reagents one after another taking a portion of this neutral solution each time:

(*vi*) $AgNO_3$ solution, (*vii*) Denige's reagent, (*viii*) $FeCl_3$ solution.

Experiment	Observation
(*ix*) *Morphine test*: Add a trace of morphine taken on a pinhead to a drop or two of the green-coloured solution taken out for the purpose (from a mixture of $K_2Cr_2O_7$, methyl alcohol and sulphuric acid). Now add excess of conc. H_2SO_4 down the side of the test-tube.	There spread immediately in the sulphuric acid layer dark-violet streaks, which ultimately becomes brown.

13. Ethyl alcohol, C_2H_5OH

Ethyl alcohol is a colourless, neutral, volatile and inflammable liquid having a characteristic pleasant and sweet smell. It is miscible with water in all proportions.

Preliminary tests

Experiment	Observation
(*i*) Heat in a dry test-tube a few drops of the liquid.	Inflammable vapours are given off and the liquid completely volatilises away.

Wet tests

Experiment	Observation
(*ii*) *Iodoform test*: To a little of the aqueous solution of alcohol taken in a test-tube add an equal volume of a conc. solution of iodine in potassium iodide. Warm a little, add dropwise a dilute solution of caustic soda or sodium carbonate till the brown colour due to iodine vanishes and finally cool.	A yellow crystalline ppt of iodoform[1] with a peculiar but characteristic odour comes down.

Oxidation of ethyl alcohol to acetaldehyde: Carry out oxidation of alcohol by acid-dichromate (or copper spiral) as indicated under methyl alcohol. Unlike methyl alcohol, in either case ethyl alcohol is oxidised to acetaldehyde. Take the smell of the oxidised liquid and recognise acetaldehyde by carrying out the following tests with the oxidised solution:

Experiment	Observation
(*iii*) Add a few drops of freshly prepared Schiff's reagent to a portion of the oxidised solution.	Development of a pink colour, which deepens gradually.

---

[1] This iodoform reaction is given by acetone also, *see* acetone for distinction between the two.

Experiments	Observations
(*iv*) To a little of the oxidised solution add about an equal volume of a very dilute solution of sodium nitroprusside and then only a few drops of a dilute NaOH solution.	Production of wine-red colour.
(*v*) *Morphine test*: Perform this test as indicated under methyl alcohol.	Yellow coloration.
(*vi*) *Piperidine test*: To 1 c.c. of the oxidised solution add about 1 c.c. of a very dilute solution of sodium nitroprusside (freshly prepared) and finally add a drop of piperidine.	Development of a deep-blue colour.

14. Glycerol, $CH_2OHCHOHCH_2OH$

It is a neutral, colourless, odourless, sweet, syrupy liquid. It is miscible with water in all proportions.

Preliminary tests

Experiments	Observations
(*i*) Heat in a clean and dry test-tube a little of glycerol.	The liquid[1] completely volatilises off, giving dense white fumes.
(*ii*) Add a little conc. H_2SO_4 to a small portion of glycerol taken in a test-tube and finally heat it by placing in a beaker of boiling water.	No change of colour in the cold, a slight yellow[2] colour may develop on warming.

---

[1] If an aqueous solution of glycerine be supplied, a syrupy residue is obtained at first, which ultimately volatilises off completely giving off dense white fumes.

[2] A distinction from sugars, which, under similar condition, undergo charring.

Experiment	Observation
(*iii*) Add a little of a 3% NaOH solution to a portion of glycerine taken in a test-tube and finally heat.	No change[1] of colour even on heating

Wet-tests

Experiments	Observations
(*iv*) *Acrolein test*: Mix a portion of the given liquid[2] with potassium hydrogen sulphate or anhydrous magnesium sulphate or zinc sulphate. Heat the resulting mixture strongly.	Bitingly acrid, *i. e.*, tear exciting odour evolves.
(*v*) Perform the above expt. in a test-tube fitted with a cork and a delivery tube and allow the evolved gas to pass through Schiff's reagent.	Pink colour develops.
(*vi*) *Dunstan's test*: Add a few drops of phenolphthalein to a very dilute solution (1%) of borax, when a pink colour develops. Now add a little of aqueous solution of the sample to it. Heat and cool again.	The pink colour of the solution vanishes[3], but the colour gradually returns on heating and disappears again on cooling.

15. Benzaldehyde, C_6H_5CHO

Benzaldehyde is a colourless, neutral liquid having the smell of bitter almonds. It is very slightly soluble in water.

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[1] Sugars under similar condition exhibit change of colour, hence a distinction.

[2] In case of aqueous solution use the thick viscous mass obtained by careful evaporation of the given solution.

[3] Though the other polyhydric alcohols and glucose do respond to this est, yet the reaction is not so pronounced as in the case of glycerol.

Preliminary tests

Experiments	Observations
(*i*) Heat in a clean and dry test-tube a little of benzaldehyde.	No residue.
(*ii*) Warm a little of benzaldehyde with conc. H_2SO_2.	The acid layer turns reddish-brown (tan).

Wet-tests

Experiments	Observations
(*iii*) Add a few drops of aldehyde to about 5 c.c. Schiff's reagent and shake.	A pink[1] colour develops slowly.
(*iv*) Dissolve a few droos of phenylhydrazine in 1 c.c. of acetic acid, add a drop of benzaldehyde and shake.	A crystalline ppt. appears.
(*v*) Add a little of the sample to 2 : 4 dinitrophenylhydrazine (*cf.* pages 118-19).	Reddish-yellow ppt. simply on mixing.
(*vi*) *Cannizzaro's reactions*: Mix a portion of the liquid with twice its volume of 30% casutic soda solution, gently warm and stir with a glass rod for five minutes. Add sufficient water and shake to dissolve out any solid that may separate out. Decant off the aqueous solution from any unchanged liquid. Acidify the decanted solution with conc. HCl and cool.	A white ppt.
(*vii*) *Malachite green*: Take in a test-tube three drops of benzaldehyde, add a drop or two of dimethylaniline and a small bit of anhydrous zinc chloride. Heat the mixture for about a minute and cool. Mix in another test-tube 3 c.c. of ethyl alcohol with two drops of conc. HCl. Treat the cooled mass with this mixture of alcohol and acid.	An intense green coloration.

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[1] Try reduction of Fehling's solution, for which *see* the tests indicated under carbohydrates. Benzaldehyde cannot reduce Fehling's solution—a distinction from formaldehyde and acetaldehyde.

16. Acetone, CH_3COCH_3

Acetone is a neutral, volatile and inflammable liquid. It is colourless and possesses a pleasant etherial odour. It is miscible with water in all proportions.

Preliminary tests

Experiments	Observations
(*i*) Heat a few drops of the liquid in a clean and dry test-tube.	The liquid completely volatilises off.
(*ii*) Warm a few drops of the liquid with conc. H_2SO_4.	At first darkening of colour and ultimately charring occurs.

Wet-tests

Experiments	Observations
(*iii*) *Iodoform reaction*: Perform this reaction with a little of aqueous solution of acetone as indicated under ethyl alcohol. (page 152).	A yellow crystalline ppt. of iodoform with a peculiar but characteristic odour comes down.
(*iv*) *Iodoform reaction in presence of weaker alkali*: To a little of the aqueous solution of acetone taken in a test-tube add an equal volume of conc. solution of iodine in potassium iodide. Warm gently, add dropwise a dil. solution of NH_4OH and shake the test-tube.	The black or brown ppt. first formed dissolves and a yellow crystalline[1] ppt. of iodoform appears slowly

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[1] The formation of iodoform in presence of weak alkali ammonia distinguishes acetone from ethyl alcohol, which under similar condition, does not give iodoform.

Experiments	Observations
(*v*) Add a little of the liquid to 2 : 4 dinitrophenylhydrazine (*cf.* pages 118-19).	Beautiful ppt. simply on mixing.
(*vi*) *Legal's test*: To 3 c.c. of an aqueous solution of acetone add a few drops of a freshly prepared dil. solution of sodium nitroprusside and then a few drops of dil. NaOH solution.	A ruby red (reddish-purple) colour develops.
(*vii*) Add an equal volume of Denige's reagent to an aqueous solution of acetone in the cold and then keep the test-tube in a beaker of boiling water for a few minutes.	No precipitation in the cold, but ppt. appears on boiling the mixture.

17. Glucose, $CHO(CHOH)_4CH_2OH$

Glucose is a colourless, odourless, crystalline solid. It is sweet to taste, soluble in water and the solution reacts neutral to litmus. It crystallises from aqueous solution with one molecule of water.

Preliminary tests

Experiments	Observations
(*i*) Heat a little of glucose in a clean and dry test-tube.	The substance melts, turns brown and gives off smell of burnt sugar.
(*ii*) Add a few crystals of glucose to cold and conc. H_2SO_4 and finally heat.	No charring occurs in the cold, which, however, takes place on heatig.
(*iii*) Add a solution of 3% NaOH to a few crystals (or a conc. solution) of gucose and heat.	The solution becomes yellow[1] and ultimately turns reddish-brown.
Acidify the above reddish-brown solution with dil. HNO_3.	The solution becomes pale-yellow and gives off smell[1] of burnt sugar.

---

[1] Note the distinction—cane-sugar solution under similar condition gives a straw colour at the most and on acidification with HNO_3 does not give off the smell of burnt sugar.

Wet-tests

Experiments	Observations
(*iv*) *Molisch's test*: Take about 1 c.c. of aqueous solution of glucose in a test-tube, add two drops of a 15% solution of α-naphthol. Now add carefully and without shaking down the side of the test-tube 2 c.c. of conc. H_2SO_4.	A blue or violet colour at the junction of two liquid layers.
(*v*) Add 2 c.c. of *Barfoed's reagent* to about 1 c.c. of the aqueous solution of glucose, mix thoroughly and place the test-tube in water kept boiling in a beaker.	A red ppt. comes down.
(*vi*) To 1 c.c. of the aqueous solution add 1 c.c. of *Fehling's solution* and subsequently heat the mixture.	A yellow ppt., which gradually turns red comes down.
(*vii*) *Osazone reaction*: To about 10 c.c. of a dilute aqueous solution (10%) of glucose add 2 c.c. each of phenylhydrazine and glacial acetic acid. Shake well and warm by placing the tube in water kept boiling in a beaker.	A yellow mass crystallises out of hot solution.
(*viii*) To a solution of glucose in a test-tube add lead acetate solution. Boil, add dil. ammonia dropwise till just sufficient to produce a permanent white ppt., and boil again.	The ppt. becomes salmon-pink in colour.

N.B. If in **Osazone reaction** phenylhydrazine hydrochloride (or sulphate) be used instead of phenylhydrazine itself, replace acetic acid by sodium acetate. Take in that case 3 gms. each of NaAc and hydrochloride (or sulphate), dissolve in water, warm and filter, if necessary. Use this solution for osazone reaction instead of phenylhydrazine and acetic acid.

18. Cane-sugar, $C_{12}H_{22}O_{11}$

Cane-sugar is a colourless crystalline solid. It is sweet to taste, soluble in water and the solution reacts neutral to litmus.

Preliminary tests

Experiments	Observations
(*i*) Heat in a dry test-tube a little of cane-sugar.	The substance first melts, then turns brown and gives off smell of burnt sugar.
(*ii*) Add conc. H_2SO_4 to a little of solid cane-sugar.	Immediate charring occurs even in the cold[1].
(*iii*) (*a*) Heat a conc, solution of cane-sugar with 3% NaOH solution.	(*a*) No change in[2] colour, a straw-yellow colour may develop at the most.
(*b*) Acidify the above mixture with dil. HNO_3.	(*b*) No smell of burnt sugar.

Wet-tests

Experiments	Observations
(*iv*) *Molisch's tests*: Perform as in the case of glucose [page 158, expt. -(iv.)]	A blue or violet colour at the junction of two liquid layers.
(*v*) To a little of the solution of cane-sugar add a solution of lead acetate and boil. Add dil. ammonia dropwise till just sufficient to produce a permanent white ppt. and boil further.	No change in colour of the ppt[3].
(*vi*) Reduction of *Barfoed's reagent*: Try this reaction with cane-sugar solution as indicated under glucose [page 158, expt. -(v).]	No. ppt.
(*vii*) (*a*) Reduction of *Fehling's solution*: Try this reaction with a solution of cane-sugar as indicated under glucose [page 158, expt.-(vi).]	No. ppt.

---

[1],[2] Note the distinction from glucose and lactose.

[3] Note the distinction from glucose and lactose. The ppt. in the case of glucose or lactose changes colour.

Experiments	Observations
(*b*) Boil for a few minutes a little of cane-sugar solution with dil. HCl or sulphuric acid. Now make the solution alkaline with caustic soda solution (test with red litmus). Add a little of Fehling's solution to the above alkaline mixture and finally heat on water both.	Red ppt. of cuprous oxide comes down.
(*viii*) *Seliwanoff's reaction*: To 2 c.c. of the solution of cane-sugar add 2 c.c. of conc. HCl and a rice grain of resorcinol. Place the test-tube in boiling water for two minutes.	A deep wine-red colour, which is usually followed by a ppt. develops. The ppt., if appears, dissolves in alcohol yielding a deep wine-red solution.

19. Lactose, $C_{12}H_{22}O_{11}$

It is a crystalline solid. It is soluble in water and the solution reacts neutral to litmus. It crystallises in rhombic prism with one molecule of water. It is sweet to taste but it is the least sweet sugar.

Preliminary tests

Experiments	Observations
(*i*) Heat in a dry test-tube a little of the solid.	The substance first melts and then turns brown giving off smell of burnt sugar.
(*ii*) (*a*) Add a little of cold conc. H_2SO_4 to a portion of the sample.	(*a*) No change in the cold.
(*b*) Warm the above mixture to about 100°C.	(*b*) Gases are evolved and the mixture turns black.

Experiments	Observations
(*iii*) (*a*) Add a little of a 3% solution of caustic soda to a conc. solution of lactose and just warm for a minute.	(*a*) No change in colour.
(*b*) Heat further.	(*b*) Solution becomes yellow and ultimately brownish-red.
(*c*) Acidify the above mixture with dil. HNO_3.	(*c*) Solution becomes colourless and a smell of burnt sugar is given off.

West-tests

Experiments	Observations
(*iv*) *Molisch's test*: See glucose [Page 158, expt. -(iv)].	A blue or violet colour at the junction of two liquid layers.
(*v*) Reaction with *lead acetate*: See glucose [page 158, expt. -(viii).]	The ppt. turns pink.
(*vi*) Try *Reduction of Barfoed's reagent*: See glucose [Page 158, expt. -(v).]	No reduction[1], indicated by the absence of a red ppt.
(*vii*) *Reduction of Fehling's solution*: See glucose [page 158, expt. -(vi).]	Red ppt.[2].
(*viii*) *Osazone formation reaction*: Same as in the case of glucose [*see* page 158, expt.-(vii)] with the only difference that after warming for 15 minutes the test-tube should be taken out from boiling water and allowed to cool.	Yellow crystals separate out *on cooling*[1].

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[1] Distinction from glucose.

[2] Distinction from cane-sugar.

20. Starch $(C_6H_{10}O_5)n$

Starch is a tasteless, odourless, white amorphous powder. It is insoluble in cold water. But, if boiled with water, it forms gelatinous mucilage, which yields a hazy* solution on dilution and the solution reacts neutral to litmus.

Preliminary tests

Experiments	Observations
(*i*) Heat in a clean and dry test-tube a little of solid starch.	Charring occurs, odour of burnt wood or leather is given off.
(*ii*) Heat with conc. H_2SO_4 a little of starch taken in a test-tube.	Rapid charring with evolution of gases takes place.

Wet-tests

Experiments	Observations
(*iii*) *Molisch's test*: See glucose [page 158, expt. -(*iv*)].	A blue or violet colour at the junction of two liquid layers.
(*iv*) Try *Reduction of Barfoed's reagent*: See glucose [page 158, expt. -(*v*)].	No red ppt.
(*v*) Try *Reduction of Fehling's solution*: See glucose [page 158, expt. (-(*vi*)].	No red ppt.
(*vi*) Add a drop of a dil. solution of iodine in potassium iodide to about 1 c.c. of the solution of starch taken in a test-tube	A blue colour develops.

21. Aniline, $C_6H_5NH_2$

Freshly distilled aniline is a colourless, oily liquid. It turns brown on exposure to light and air and it is for this reason that aniline is often found to be present in this form in our laboratories. It is slightly soluble in water but it forms with acids, crystalline salts, which are soluble in water. It has a characteristic nauseating odour.

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*There is a variety, which gives clear solution on boiling with water.

Preliminary tests

Experiment	Observation
(*i*) Heat in a dry test-tube a little of aniline and ignite the the issuing gas.	The substance completely volatilises away. The evolved vapours burn with a smoky flame.

Wet-tests

Experiments	Observations
(*ii*) Add a solution of bleaching powder to a dilute solution of aniline or of one of its salts.	Purple-violet colour, which turns green on standing.
(*iii*) Take a drop of aniline itself (or a dilute solution of aniline salt) and add distilled water to make the test-tube almost full. Shake and add bromine water little by little.	A copious white ppt.
(*iv*) *Diazo reaction and coupling*: See page 124, expt. -(*f*).	An immediate brilliant scarlet-red ppt. or coloration.
(*v*) *Carbylamine reaction*: See page 124, expt.-(*e*).	A characteristic obnoxious odour.

22. Dimethylaniline, $C_6H_5N(CH_3)_2$

Freshly distilled dimethylaniline is a colourless, oily liquid. It is insoluble in water and has a characteristic nauseating odour. It forms salts with acids, which are soluble in water.

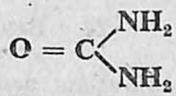
Preliminary tests

Experiment	Observation
(*i*) Heat in a dry test-tube a little of the liquid.	The liquid completely volatilises away.

Wet-tests

Experiments	Observations
(*ii*) Dissolve a little of the liquid in dil. HCl and add a little of a solution of potassium ferrocyanide.	A white crystalline ppt. appears.
Boil the above mixture.	The ppt. dissolves.
(*iii*) *Formation of malachite green*: See benzaldehyde, page 155, expt. -(*vii*).	Same as with benzaldehyde.
(*iv*) *Formation of azo-colour*: Add a little of dil. HCl to a portion of the given liquid. Cool under tap. In another test-tube take a few drops of aniline and dissolve it in dil. HCl. Cool and add in portions an aqueous solution of sodium nitrite. Cool the solution again and pour a little of it into the first (*i.e.*, solution of dimethylaniline in HCl) solution and allow to stand.	A beautiful rose-red colour develops.
(*v*) *Formation of p-nitroso dimethylaniline*:	
(*a*) Add a little of dil. HCl to a portion of the given liquid. Cool under tap. Add about one-third of the total volume of this mixture a strong aqueous solution of sodium nitrite.	(*a*) A red colour (some times a white ppt.) develops.
(*b*) Filter, if any ppt. and add on to the ppt. a little of a dil. solution of caustic soda. If, on the other hand, no ppt. be obtained on addition of sodium nitrite, make the solution alkaline by adding dil. solution of caustic soda.	(*b*) The ppt. turns green; *or*, a green solution results.

23. Urea,



$$O=C\begin{matrix}NH_2\\NH_2\end{matrix}$$

Urea is a colourless, crystalline solid, highly soluble in water.

Preliminary tests

Experiments	Observations
(*i*) Heat a small quantity of urea in a clean and dry test-tube.	Smell of ammonia is perceived, and on strong heating a white sublimate is formed on cooler parts of the test-tube.
(*ii*) Heat gently about $\frac{1}{8}$th inch layer of the solid, until the melted mass just solidifies, when taken out of the flame. Cool, dissolve the residue in 1 c.c. of dilute caustic soda solution by shaking and warming. Cool and finally add a drop or two of a *very dilute* copper sulphate solution.	A pink or *violet* colour develops.

Wet-tests

Experiments	Observations
(*iii*) (*a*) Acidify a portion of the solution of urea with dil. HCl, add about 3 c.c. of a $2\frac{1}{2}\%$ aqueous solution of sodium nitrite and shake.	(*a*) Effervescence takes place.
(*b*) Take a drop of baryta water at the tip of a glass rod and hold it over the mouth of the test-tube.	(*b*) Baryta water turns milky.
(*iv*) Take a little of the solution of urea in a test-tube and add about 2 c.c. conc. nitric acid to it. Concentrate[1] the mixture by boiling and cool.	A white crystalline ppt. appears; ppt. is soluble in water.
(*v*) Take a little of the solution of urea. Add conc. solution of oxalic acid to it. Concentrate[1] by boiling and cool.	A white crystalline ppt. sparingly soluble in water.

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[1] If concentrated solution of urea be taken, further concentration by boiling is unnecessary; ppt. will appear simply on cooling the hot mixture.

24. Benzene, C_6H_6

Benzene is a colourless, neutral, volatile liquid. It possesses a peculiar odour. It is inflammable and burns with a sooty flame. It is immiscible with water.

Preliminary tests

Experiments	Observations
(*i*) Heat a small quantity of the liquid in a dry test-tube.	The liquid completely volatilises off.
Ignite the issuing vapours.	The vapours burn with a smoky flame.
(*ii*) Add conc. H_2SO_4 to a portion of the liquid in cold.	No change[1] in colour.

Wet-tests

Experiment	Observation
(*iii*) Add slowly and dropwise 2 c.c. of the given liquid to twice its volume of sulphuric-nitric acid mixture (conc. H_2SO_4 and conc, HNO_3 are to be mixed in the proportion of 2 : 1 by volume) taken in a small beaker, which is kept cold by placing in a bath of cold water. Shake the acid mixture while adding the given liquid. When addition is over, heat the mixture for about five minutes on a water-bath and pour it into an excess of water.	Oily drops having the odour of bitter almonds separate out. The oil is yellow in colour and being heavier than water collects at the bottom of the vessel under water.

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[1] Commercial benzene (impure benzene) may turn brown due to presence of thiophen C_4H_4S as an impurity.

25. Nitrobenzene, $C_6H_5NO_2$

Nitrobenzene is a pale yellow oily liquid. It resembles the smell of oil of bitter almond. It is immiscible with water.

Preliminary tests

Experiments	Observations
(*i*) Heat a small quantity of the liquid in a test-tube.	The liquid completely volatilises away giving off vapours[1].
(*ii*) Mix a conc. solution of caustic soda with a portion of the liquid in a test-tube and heat the mixture.	The colour darkens.

Wet-tests

Experiments	Observatins
(*iii*) *Mulliken and Barker's* test: *See* page 124.	A black or grey ppt.
(*iv*) Reduce with tin and hydrochloric acid and then perform:	
(*a*) *Carbylamine reaction* and	(*a*) A characteristic obnoxious odour.
(*b*) *Diazo-reaction and coupling*. See page 124.	(*b*) A brilliant scarlet-red ppt. or coloration.

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[1] *Don't* inhale, as it is *poisonous*.

26. Chloroform, $CHCl_3$

Chloroform is a colourless, volatile, non-inflammable liquid. It is neutral to litmus and possesses a sweet sickly smell. It is practically insoluble in water.

Preliminary tests

Experiments	Observations
(*i*) (*a*) Heat a small quantity of chloroform in a dry test-tube.	The liquid completely volatilises off.
(*b*) Allow the issuing vapours to come in contact with a non-luminous Bunsen flame.	The flame becomes green in colour.

Wet-tests

Experiments	Observations
(*ii*) Add Fehling's solution to a small quantity of chloroform and warm with constant shaking.	A yellowish-red ppt. comes down.
(*iii*) Take a little of powdered resorcinol in a test-tube, add a few drops of chloroform to it. Now add about 1 c.c. of a strong solution of caustic soda and warm gently.	A brilliant red colour develops in the aqueous layer.
(*iv*) Perform *Carbylamine reaction* : *See* page 124, expt.-(*e*).	A characteristic obnoxious odour.

CHAPTER II

IDENTIFICATION OF AN ORGANIC SAMPLE

(containing one of the commonly known compounds)

The sample supplied may be a pure solid or liquid or its aqueous solution or a solution of its salt.

Introduction

Keeping in view the limitations of the syllabi of different universities, which include the detection of one of the common organic compounds, the discussion here will be confined to the treatment of compounds listed below:

(*a*) Methyl alcohol, (*b*) Ethyl alcohol, (*c*) Acetone, (*d*) Aniline, (*e*) Dimethylaniline, (*f*) Acetic acid, (*g*) Formic acid, (*h*) Benzoic acid, (*i*) Salicylic acid, (*j*) Oxalic acid, (*k*) Citric acid, (*l*) Tartaric acid, (*m*) Succinic acid, (*n*) Cane-sugar, (*o*) Glucose, (*p*) Lactose, (*q*) Starch, (*r*) Chloroform, (*s*) Benzene, (*t*) Phenol, (*u*) Glycerol, (*v*) Benzaldehyde, (*w*) Nitrobenzene, (*x*) Betanaphthol, (*y*) Urea.

SAMPLE

Solid		*Liquid*	
Pure organic compound	Salts	Pure organic compound	Solution
Benzoic acid, Salicylic acid, Oxalic acid, Citric acid, Tartaric acid, Succinic acid, Cane-sugar, Glucose, Lactose, Starch, Urea, Betanaphthol.	Salts *of acids, aniline, dimethyl aniline, urea, and of phenols.	Methyl alcohol, Ethyl alcohol, Acetone, Aniline, Dimethylaniline, Acetic acid, Formic acid Chloroform, Benzene, Phenol, Glycerol, Benzaldehyde, Nitrobenzene.	Aqueous solution of salts* and of all pure organic compounds excepting the following: Benzoic, Salicylic, Succinic Betanaphthol, Aniline, Dimethylaniline, Chloroform, Benzene, Benzaldehyde, Nitrobenzene.

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*By salts sodium, potassium or ammonium salts of the acids, hydrochlorides and sulphates of amines, nitrate of urea and alkali salts of phenols are meant here.

If, therefore, the given sample be a solid, then methyl alcohol, ethyl alcohol, acetone, chloroform, glycerol, benzaldehyde, benzene, nitrobenzene, free formic and acetic acids, free aniline and dimethylaniline are definitely absent.

If, on the other hand, the sample given for analysis be in the liquid state (a pure liquid or an aqueous solution of a liquid or solid), then any one of all the above compounds or a salt of one of them may be present. But when an aqueous solution (if their be any such positive hint or direction) is given for analysis, benzene, benzaldehyde, nitrobenzene, chloroform, free aniline and dimethylaniline are definitely absent. This is because of the fact that these compounds are insoluble in water and consequently immiscible with it. Note also that phenol and betanaphthol are sparingly soluble in water. Besides, succinic acid is moderately soluble in cold water. Benzoic acid and salicylic acid are sparingly soluble in cold water but readily soluble in hot water. With hot water starch gives a hazy solution (there is also a soluble variety of starch, which gives a clear solution in water) and when a portion of it is treated with a drop of iodine the colour of the solution changes to blue black.

Colour, odour and solubility of the given sample may serve an indication as to the presence or absence of one or the other compound. Nitrobenzene, for example, is a pale yellow oily liquid and, in fact, of the substances included in the list it is the only coloured substance. It should, however, be noted that phenols and amines are often found to possess various shades of colour. This is either because of the presence of impurities in the sample or due to some foreign substances being formed by aerial oxidation of the pure substance. Odour of an organic compound may sometimes indicate the nature of the compound and thus acts as a guide. Alcoholic smell, for example, indicates the presence of either methyl or ethyl alcohol. Besides, acetone, acetic acid, aniline, chloroform, benzene, benzaldehyde, nitrobenzene, phenol, dimethylaniline, etc.—all have characteristic odour.

Behaviour of the organic sample towards litmus paper also gives a positive indication regarding the nature of the substance.

If acidic, the sample given for analysis may contain free acids (*e.g.*, formic, acetic, oxalic, etc.), acid salt, some ammonium salts of organic acid, phenol, salts of aniline, dimethyl aniline and of urea.

If no action on (or neutral to) litmus, the sample may contain alcohols, acetone, chloroform, benzene, starch, benzaldehyde, betanaphthol, nitrobenzene, glycerine, sugars, urea, aniline, dimethylaniline and normal salts of acids.

If basic, the sample may contain some salts specially those of sodium and potassium of weak organic acids and phenolates.

Scheme

Before entering into actual analysis, the physical characteristics of the sample must be noted. Observe whether the sample is a solid or liquid and note its colour and odour. Observe whether the sample is soluble in water or not and note the behaviour of the resulting solution or suspension towards litmus paper. Observe the solubility of the sample in dilute solutions of sodium bicarbonate, sodium hydroxide and hydrochloric acid in succession. *In the case of liquid* sample (a pure liquid or solution of a solid or liquid) observe also the change that may occur when a portion of the given liquid is carefully evaporated to dryness and draw the inference therefrom.

After the completion of the above introductory observations either the *procedure A* or the *procedure B*, whichever is applicable, is to be followed.

Follow the *procedure A*, whenever a solid sample is given or if the given liquid sample (a pure liquid or solution of a solid or liquid) leaves a residue on careful evaporation. Sufficient informations being obtained thereby. the next step in this type of qualitative analysis is to carry out the necessary confirmatory reactions in order to detect the compound already suspected.

If, however, no residue is obtained on careful evaporation of a portion of the given liquid, follow the *procedure B*.

Introductory Experiments

Experiments	Observations	Inferences
I. Note the state of aggregation, colour and odour of the given sample.	...	...
II. Shake a portion of the sample with a little water in a test-tube.	(*a*) Substance dissolves.	(*a*) Water-soluble substances.
	(*b*) Substance does not dissolve.	(*b*) Water-insoluble or immiscible substances.
III. Test the resulting aqueous solution or suspension obtained in above expt. (*i.e.*, expt. -II) with litmus paper.	(*a*) Blue litmus turns red.	(*a*) Acidic substances.
	(*b*) Red litmus turns blue.	(*b*) Basic substances.
	(*c*) No action on litmus paper.	(*c*) Neutral substances.
If the substance is sparingly soluble (expt.-II) in cold water and the resulting mixture reacts acidic (expt.-III). heat the mixture.	The substance dissolves.	Benzoic acid salicylic acid.

IV. Repeat the expt.-II as stated above, substituting water by dilute solution of : (*a*) bicarbonate, (*b*) caustic soda and (*c*) hydrochloric acid in succession.

Observations	Inferences
(*a*) (*i*) Substance dissolves	(*i*) Water-soluble substances, Benzoic acid and Salicylic acid.
(*ii*) Oil separates out	(*ii*) Amine-salts.
(*b*) (*i*) Substance dissolves	(*i*) Water-soluble substances, Bicarbonate soluble substances, phenol and Betanaphthol.
(*ii*) Oil separates out	(*ii*) Amine-salts, Benzaldehyde.
(*iii*) Brown resinous mass on slight heating	(*iii*) Carbohydrates.
(*c*) (*i*) Substance dissolves	(*i*) Water-soluble substances, Aniline and Dimethylaniline.
(*ii*) White ppt.	(*ii*) Benzoate, Salicylate, Succinate and salt of Betanaphthol.
(*iii*) Oil separates out	(*iii*) Salt of Phenol.

V. Whatever be the nature of the sample, if it is supplied in the liquid state (a pure liquid or its solution or solution of a solid), evaporate a portion of the sample to dryness by careful heating in a clean basin over a small flame. A liquid sample (pure liquid or its solution or solution of a solid) may leave on evaporation:

(*i*) *Solid residue*	(*ii*) *Syrupy residue.*	(*III*) *No residue.*
(*a*) Sample, if reacts *acidic*; free organic acids (excluding formic and acetic), salts of aniline, dimethylaniline and of urea, amonium acetate.	(*a*) Sample reacts slightly *acidic* (almost neutral); phenol[2].	(*a*) Same reacts *neutral* to litmus, methyl alcohol, ethyl alcohol, acetone, chloroform,* benzene,* nitrobenzene,* benzaldehyde,* glycerine[3], aniline,*[4] and dimethylaniline*.
(*b*) Sample, if reacts *neutral*; urea[1], salts of acids.	(*b*) Sample reacts *neutral*; glucose, cane-sugar, lactose, starch, glycerine[3].	(*b*) Sample reacts *acidic*; acetic acid formic acid, phenol[2] (slightly acid).
(*c*) Sample if reacts *alkaline*; phenolates and sodium-potassium salts of weak organic acids.		

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[1] Urea is a very weak base.

[2] Phenol is partially soluble in water and the aqueous solution leaves a reddish syrupy residue on evaporation. But pure phenol on strong heating volatilises away completely and the characteristic 'carbolic odour' is given off.

[3] The residue ultimately volatilises away, dense white fumes are evolved (leaving simply a black streak).

[4] Pure aniline volatilises away completely, giving off white choking fumes, which, if burnt produce a sooty flame.

*Marked samples are *immiscible with water*.

Procedure A

Sample given is a solid or the given liquid sample leaves a residue on careful evaporation.

In such a case perform at this stage the following *preliminary experiments* more or less in the order given below.

Expt. I. Heat a little of the given solid or residue obtained on evaporation gently in a hard glass test-tube.

Observations	Inferences
(*a*) *No charring*, but gives off odour of:	
(*i*) ammonia	Urea, ammonium salts of acids.
(*ii*) aniline (like)	Salts of aniline or dimethylaniline.
(*iii*) phenol	Phenate, salicylate.
(*iv*) vinegar	Acetate
(*v*) irritating fumes	Succinate
(*vi*) irritating fumes having aromatic odour	Benzoate
(*b*) *Charring occurs* with the evolution of:	
(*i*) smell of burnt sugar	Sugars (glucose, sucrose, lactose), tartrate.
(*ii*) Smell of burnt wood or leather	Starch
(*iii*) acrid vapours	Citrate
(*iv*) the substance chars slightly and yields a white sublimate.	Salt of aniline

Expt. II. Warm a portion of the solid or the residue or the concentrated solution* with dilute sulphuric acid in a test-tube.

Observations	Inferences
(*i*) Acid fumes with pungent odour are evolved.	Formate
(*ii*) Acid fumes having the odour of vinegar are evolved.	Acetate

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*If the sample given for analysis be a solution, which, on acidification with dil. H_2SO_4, gives a white ppt., then the sample in all probability is either a benzoate or a salicylate.

Expt. III. Repeat the above expt. (*i.e.*, expt. -II) with conc. sulphuric acid instead of dilute acid.

Observations	Inferences
(*a*) *Immediate blackening occurs* and the substance gives off gases.	Sugars, Tartrate, Starch.
(*b*) *No immediate blackening*, which occurs only slowly with the evolution of gases.	Citrate, salicylate.
(*c*) *No blackening at all.*	
(*i*) The evolved gas burns with a blue flame at the mouth of the test-tube.	Formate
(*ii*) The evolved gas when passed through lime water, the latter turns milky.	Oxalate
(*iii*) Acid fumes having (*a*) irritating aromatic odour, (*b*) odour of vinegar are evolved.	(*a*) Benzoate; (*b*) Acetate

Expt. IV. Mix the solid or the residue obtained on evaporation with 3-4 times of its weight of dry sodalime and heat the resulting mixture strongly in a hard glass test-tube.

Observations	Inferences
(*i*) Odour of benzene, the evolved vapours burn *with a smoky flame.*	Benzoate
(*ii*) Odour of ammonia is evolved.	Urea, ammonium salts.
(*iii*) Odour of phenol is evolved	Phenol, salicylate.
(*iv*) Vapour having aniline like odour is evolved.	Salts of aniline and dimethyl aniline.

Expt. V. Heat the solid or residue with zinc dust in a hard glass test-tube.

Observations	Inferences
(*i*) Vapours smell like petrol and burn with a sooty flame.	Phenol
(*ii*) Smell of naphthalene evolves and a white sublimate gets deposited on the cooler parts of the test-tube.	Betanaphthol

Wet Reactions

When the preliminary observations (*i.e.*, physical characteristics, action towards litmus, etc. and preliminary reactions) indicate the presence of salts of aniline or dimethylaniline proceed directly with the reaction under expt. -(*iv*) in page 163 and expts. -(*iii*), (*iv*) and (*v*) in page 164 to confirm its presence. Similarly, whenever the presence of any one of the carbohydrates or glycerol is indicated in the preliminary observations (namely neutral action towards litmus, syrupy residue on evaporation, charring, etc.), carry out *Molisch's test*.

If Molisch's test is positive,—perform the tests for individual carbohydrates (pages 180-181).

If it is not positive, test for glycerol [expts. -(*iv*) and (*vi*) in page 154]. But in absence of such positive indications, the wet reactions as a method of routine analysis should be carried out with the neutral and concentrated solution.

Carry out the wet reactions with the neutral or neutralised (for the procedure of neutralisation *see* page 135 along with the foot-note given there) solution more or less in the order stated below.

Expt. I. To a little of the solution taken in a test-tube add dilute sulphuric acid.

Observation	Inference
A white crystalline precipitate, which dissolves on boiling but reappears on cooling, is obtained.	Benzonate, Salicylate

Expt. II. To a little of the solution or suspension—taken in a test-tube add a drop or two of a freshly prepared neutral ferric chloride solution and note immediately the change ofc olour that might have taken place.

Observations	Inferences
(*i*) Red colour is developed	Formate, Acetate.
(*ii*) Violet colour is developed—	
(*a*) Colour discharged on addition of acetic acid.	Phenol
(*b*) not discharged by acetic acid.	Salicylate
(*iii*) *A green coloration and afterwards a flocculant ppt.	Betanaphthol
(*iv*) A buff-coloured precipitate—	
(*a*) buff-colour disappears and instead a white crystalline ppt. appears on acidifying with dil. HCl.	Benzoate
(*c*) buff colour disappears but no white ppt.	Succinate

Expt. III. To a portion of the neutral solution and an equal volume of calcium chloride solution.

Observations	Inferences
(*i*) An immediate white ppt. which does not dissolve in acetic acid.	Oxalate
(*ii*) A sand-like ppt. on shaking and scratching the inside of the tube—	Tartrate, succinate
(*a*) ppt. insoluble in acetic acid:	Mesotartrate
(*b*) ppt. soluble in acetic acid	Succinate *d*-tartarate),
(*iii*) No ppt. even on shaking and scratching but on boiling only.	Citrate

Expt. IV. Add cadmium chloride solution to a portion of the neutral solution taken in a test-tube.

Observations	Inferences
(*i*) Preciptaition occurs in cold or on heating—ppt. is white and gelatinous.	Citrate
(*ii*) Precipitation occurs specially after heating—ppt. is white and crystalline.	Oxalate

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*The colour becomes more pronounced, when the test is carried out with alcoholic solution.

Expt.-V. Add an equal volume of Denige's reagent to a little portion of the original solution* (taken in a test-tube) in the cold.

Observations	Inferences
(*a*) An immediate white ppt:	
(*i*) which dissolves on boiling	Benzoate, salicylate.
(*ii*) which does not dissolve on boiling	Oxalate
(*b*) No precipitation in the cold but precipitate appears on boiling the mixture.	Formate, acetone†
(*i*) white sandy ppt. which comes down during the course of boiling.	Formate
(*c*) No precipitation even on boiling the mixture, but	
(*i*) a white ppt. or turbidity appears on adding to the hot mixture a drop or two of a 2% solution of potassium permanganate, the colour of which is discharged.	Citrate
(*ii*) colour of permanganate is not discharged and no ppt. or turbidity comes down.	Succinate, acetate, urea.

Expt.-VI. Cary out *Molisch's test* as indicated under glucose in page 158.

Observation	Inference
A blue or violet colour at the junction of two liquid layers.	Carbohydrates

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*If a solid sample be given, shake about one gram of the solid with 10 c.c. water, heat and filter, if necessary.

†Acetone on evaporation leaves no residue, hence the case of acetone does not arise here at all.

Confirmatory reactions

Sufficient indications having veen obtained about the possibility of one substance or the other, the next step in qualitative analysis is to recognise the substance by carrying out the individual characteristic reactions. But it should be noted here that certain substances (*e.g.*, oxalic, citric, etc., and so also their salts) do not require any additional test. If such a substance be supplied for analysis the reaction stated earlier will stand as a sufficient proof for its presence.

Carry out one or more of the following experiments as may be necessary to confirm the substance already suspected:

(*i*) If a *formate* or *acetate* be indicated, (α) try the reaction with *mercuric chloride* [pages 137,138; expt.-(VI)].

(*a*) A white ppt.—*Formate*
(*b*) No white ppt.—*Acetate*

(β) Perform the reaction with silver nitrate [pages 137, 138: expt.-(V)].

(*a*) A black ppt. comes down or the solution turns black—*Formate*

(*b*) A white ppt., which does not turn black on boiling—*Acetate*; confirm by *cacodyl oxide test* (page 137).

(*ii*) In case of *Phenol,* (α) try the reaction with bromine water [page 147; expt. -(IV)].

(β) Carry out *Liebermann's reaction* (page 147) with a drop of the given pure liquid (or a little of its concentrated solution).

(*iii*) *Betanaphthol* : Note that the ferric chloride test described earlier will stand as a sufficient proof for the presence of β-naphthol, since no compound (included in the list) other than this produces a green colour with ferric chloride solution. If, however, a green colour is produced with ferric chloride, adduce further evidence by performing the expts. -(IV), (V) and (VI) described under betanaphthol in page 149.

(*iv*) When *salicylic acid* or *a salicylate* is indicated, (α) carry out the reaction with bromine water [page 146; expt.-(VI)] and then (β) confirm by carrying out *oil of wintergeen test* [page 146; expt.-(IV)] with 0·1g. of the solid (original solid or the residue obtained on evaporation of the given solution).

(*v*) If *Succinic acid* or a *succinate* be indicated perform the *Fluorescein test* (page 140) to confirm your findings.

(*vi*) If *tartaric acid* or *a tartrate* be indicated, try the *Mirror test* and *Fenton's test* (page 142) to confirm its presence.

(*vii*) When *urea* or an *ammonium compound* or a *salt of amine* (aniline or dimethylaniline) is indicated, (*α*) warm a portion of the original solution (or the given solid) with sodium hydroxide solution.

(*a*) Strong pungent smell of ammonia—*ammonium compounds* or *urea.*

(*b*) Aniline like odour—salt of *aniline* or *dimethylaniline*; distinguish one amine from the other by carrying out individual characteristic reactions with portions of the given solution (or with portions of the solution of the given solid in water)—*Diazo-reaction* (page 124) for aniline; *formation of azo-colour, p-nitroso dimethylaniline* and *malachite green* (page 164) for dimethylaniline.

(*β*) If smell of ammonia be perceived on warming with sodium hydroxide, try the reaction with nitrous acid [page 165; expt.-(III)].

(*a*) Effervescence occurs, evolved gas turns lime water or baryta water milky—*Urea,* confirm by *Biuret* reaction [expt.-(II)] and by expts.-(IV) & (V) described in page 165.

(*b*) Lime water or baryta does not turn milky—*ammonium compound.*

(*viii*) *Examination of carbohydrates*: If the Molisch's test is positive, try the following reactions with portions of given solution (or aqueous solution of the given solid).

(*a*) Reaction with a *dil. solution of iodine in potassium iodide* [page 162; expt.-(VI)].

—a positive result—*Starch.*

(*b*) Reduction of Fehling's solution [page 158; expt.-(VI)].

(*α*) Reduction takes place, there appears a red ppt. of cuprous oxide—*Glucose or lactose**.

(*β*) No reduction, indicated by the absence of a red ppt. —*cane-sugar* or *starch.*

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*Cane-sugar solution, if kept for sometime undergoes inversion and hence a red ppt. may sometimes be obtained even when no glucose or lactose is present. In such a case add an excess of Fehling's solution and boil till the precipitation is complete. Filter off the ppt. Make the filtrate acidic with dil. H_2SO_4 or HCl. Boil for a few minutes and add caustic soda till the mixture becomes alkaline (test with litmus). Now add a little more of Fehling's solution and warm on water-bath, when a red ppt, indicates cane-sugar or starch.

(*c*) If there is reduction of *Fehling's solution*, perform the reaction with *Barfoed's reagent* (page 158).

(α) Reduction takes place, a red ppt. of cuprous oxide comes down—*Glucose.*

(β) No reduction—*Lactose*, adduce further evidence by performing the expt.-(VIII) described in page 161.

(*d*) If there is no reduction of Fehling's solution, try hydrolysis and subsequent reduction of *Fehling's solution* [page 160; expt. -(VII) *b*.]

—Red ppt. of curprous oxide comes down—*Cane-sugar*, adduce further evidence by performing *Seliwanoff's reaction* (page 160).

(*ix*) *Glycerol*: When glycerol is indicated, confirm by performing *acrolein test* and *Dunstan's test* (page 154).

Procedure B

A liquid (pure liquid or its solution) is given for analysis and the same on evaporation leaves no residue.

The substances that come under this class are:

(*i*) Methyl alcohol, ethyl alcohol, acetone, formic acid, acetic acid and glycerine.*

(*ii*) Chloroform, benzene, benzaldehyde, nitrobenzene, aniline, dimethylaniline and phenol.*

All the above compounds save and except glycerine possess a characteristic odour, with which the students must have an acquaintance through practice.

Of the above substances the first six are soluble in water, *i.e.*, they mix with water in all proportions but the rest are insoluble in water and hence, when shaken with water and allowed to stand *separation of two layers* occurs. Moreover, some of these substances react neutral, and some acidic towards litmus paper (*see* the case of *no residue* under experiment-V, page 173, decribed in introductory experiments).

When the presence of any one of the above substances is indicated by introductory experiments (*i.e.*, by its solubility, action towards litmus, characteristic colour, odour etc.)

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*Phenol and glycerine may sometimes evaporate away leaving no residue but a faint stain.

described earlier, confirm the substance suspected by carrying out its individual characteristic reactions. Note that whenever a very dilute solution is supplied for analysis, these reactions should be carried out with the solution after proper concentration.* Note also that the substances (except phenol), which are immiscible with water, if supplied, will be in the pure state and consequently the question of concentrating them does not arise at all.

Sample mixes in all proportion with water and is neutral to litmus; the sample must be one of the following: (*a*) Methyl alcohol, (*b*) ethyl alcohol, (*c*) acetone and (*d*) glycerine. Of the substances indicated, glycerine is an odourless, syrupy liquid. Confirm by acrolein test and Dunstan's test (*cf.* page 154). The other three liquids have characteristic odour. Alcoholic smell indicates either of the alcohols, whereas acetone possesses a characteristic pleasant smell. Hence when the sample has an odour perform the following experiments:

(*iα*) *Iodoform reaction* in presence of NaOH or Na_2CO_3 (page 152).

(*a*) A yellow crystalline ppt. of iodoform with a peculiar and characteristic odour comes down—*Acctone, Ethyl alcohol.*

(*b*) No ppt. and no odour—probably *Methyl alcohol*; oxidise a portion of the sample by copper coil (page 150) and carry out Schiff's, *Rimini's* and *Resorcinol tests* (page 150). Oxidise again another portion of the sample by $K_2Cr_2O_7+H_2SO_4$ (page 151) and carry out the reactions with *neutral ferric chloride solution* [page 136; expt.-(IV)], *silver nitrate soution* [page 137; expt.-(V)] and *mercuric chloride* solution [page 137; expt.-(VI)]. Adduce further evidence by carrying out *oil of wintergreen test* (page 146) and *morphine test* (page 151).

(*iβ*) If the iodoform reaction described above gives a positive result, try again the same reaction in presence of NH_4OH instead of caustic soda (or sodium carbonate).

(*α*) A positive result—*Acetone*†. adduce further evidence by carrying out *Legal's test* and reaction with 2 : 4 *dinitrophenylhydrazine* (page 157).

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*In case of volatile substances necessary concentration is attained by distillation. Glycerine solution may however be concentrated by simple boiling.

†Test with Denige's reagent may well be tried here, when a white powdery ppt. appears after some boiling indicating the presence of acetone.

(*b*) No iodoform— probably *Ethyl alcohol; oxidise the sample either by* acid dichromate or by copper coil (page 152) and confirm by carrying out *piperidine test, nitroprusside test* (*page* 153) and reaction with 2 : 4 *dinitrophenylhydrazine.* Adduce further evidence by carrying out *morphine test* (page 153).

Sample mixes in all proportion with water and the solution acidic to litmus: the sample must be either formic acid or acetic acid. Vinegar-like smell indicates acetic acid whereas pungent smell indicates formic acid. Neutralise a portion with sodium carbonate. Divide the neutral solution into two parts. Evaporate one part to dryness, carry out with the residue thus obtained the preliminary tests (pages 174-176); with the other part of the neutralised solution, carry out wet reactions (pages 176-178) and ultimately confirm your findings by performing the tests as indicated in page 179.

Given liquid is immiscible with water and the suspension *neutral to litmus*; the sample must be one of the following: Chloroform, benzene, benzaldehyde, nitrobenzene, aniline and dimethylaniline, of which the last two are soluble in dil. HCl.

Leaving aside the last two let us for the present consider the remaining four compounds. Of these chloroform and benzene are highly volatile; when a few drops of the liquid are heated in a test tube it *rapidly* volatilises away completely. Each of these substances has a characteristic odour. Chloroform possesses a sweet sickly smell, while benzene has a petrol-like odour. The odour of benzaldehyde and nitrobenzene resembles to that of bitter almonds. Besides, of the two substances benzaldehyde is a colourless while nitrobenzene is a pale yellow liquid. Hence, when the presence of any one of the above substances is indicated by its colour, odour, etc. recognise the substance by carrying out its individual characteristic reaction described below:

(*i*) If chloroform is indicated, confirm it by carrying out *carbylamine reaction* [page 124, expt. (*e*)].

(*ii*) When benzene is indicated, confirm it by *nitrobenzene test* (page 166).

(*iii*) It has already been stated when the odour of the sample resembles to that of bitter almonds either benzaldehyde or nitrobenzene is present. Colour of the sample may act here as a guide. In such a case, however, carry out the following reactions:

(*a*) Perform the test with 2 : 4 dinitrophenylhydrazine (*see* page 155), a positive result indicates benzaldehyde; confirm by *Cannizzaro's reaction* (page 155).

(*b*) *Test for nitrobenzene.* Carry out the test for nitro group (*see* page 124-125), the presence of which confirms the presence of nitrobenzene, no other nitro-compound being included in the list.

Hence, *if the liquid is immiscible with water, reacts neutral towards litmus and is soluble in dil. HCl*; the substance given for analysis must be one of the following: Aniline and dimethylaniline. Both aniline and dimethylaniline possess characteristic odour. Try, however, the individual characteristic reactions (page 180) to recognise the substance.

N.B. Note that while reporting the presence of a free acid it should be borne in mind that in such a case the aqueous solution or suspension as the case may be of the given substance must react acidic to litmus.

Explanation of Some of the Reactions performed for Detecting Organic Compound

1. Formic acid: (*a*) The acid and its salts are decomposed by conc. H_2SO_4 into carbon monoxide and water. The latter is absorbed by H_2SO_4 and the former, if ignited, burns with a blue flame.

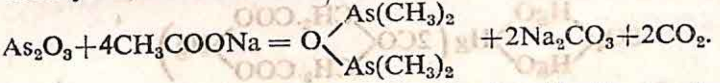
$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O;$$

$$HCOONa + H_2SO_4 \longrightarrow CO + H_2O + NaHSO_4.$$

(*b*) The acid and its salts reduce both *silver nitrate* and *mercuric chloride*. Silver nitrate is reduced to metallic silver and the mirror or the black ppt. as the case may be is due to this metallic silver. $HCOOH + AgNO_3 = HCOOAg + HNO_3$, $2HCOOAg = 2Ag + HCOOH + CO_2$. Mercuric chloride is first reduced to mercurous chloride (a white ppt.), which with more of formic acid or formate undergoes further reduction to grey metallic mercury. Hence with excess of formic acid or a formate a grey metallic deposit is ultimately obtained.

$2HCOONa + 2HgCl_2 = Hg_2Cl_2 + 2NaCl + CO + CO_2 + H_2O$;
$Hg_2Cl_2 + 2HCOONa = 2Hg + 2NaCl + H_2O + CO + CO_2$.

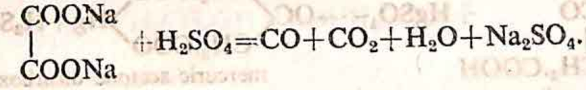
2. Acetic acid: (*a*) The extremely nauseating odour in *Cacodyl oxide reaction* is due to formation of cacodyl oxide.



$$As_2O_3 + 4CH_3COONa = O\begin{matrix} \diagup As(CH_3)_2 \\ \diagdown As(CH_3)_2 \end{matrix} + 2Na_2CO_3 + 2CO_2.$$

(*b*) The red coloration with *ferric chloride* is due to formation of ferric acetate, which, on heating, is converted into a brown ppt. of basic ferric acetate. Similar reactions occur with a formate. $3CH_3COOK + FeCl_3 = (CH_3COO)_3Fe + 3KCl$; $(CH_3COO)_3Fe + 2H_2O = \underset{\text{brown ppt.}}{(CH_3COO)Fe(OH)_2} + 2CH_3COOH$.

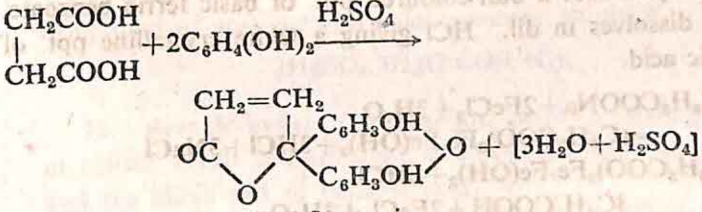
3. Oxalic acid: On heating oxalic acid or an oxalate with conc. H_2SO_4 carbon monoxide and dioxide are evolved. The presence of carbon dioxide in the issuing gas is indicated by its capability of turning lime water milky.



$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2SO_4 = CO + CO_2 + H_2O + Na_2SO_4.$$

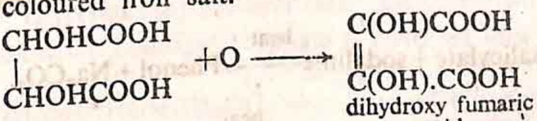
4. Succinic acid: (*a*) *Ferric chloride* solution produces with a succinate a buff-coloured ppt. of basic ferric succinate, which dissolves in dilute hydrochloric acid.
$3(CH_2COONa)_2 + 2FeCl_3 + 2H_2O$
$= (CH_2COO)_2Fe(OH) + (CH_2COOH)_2 + 6NaCl$.

(*b*) In *fluorescein test*, succinyl fluorescein is formed.



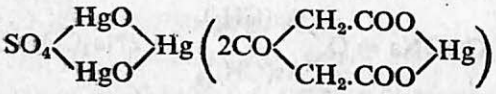
succinyl fluorescein

5. Tartaric acid: *Fenton's tests.* With ferrous salts and hydrogen peroxide it yields dihydroxy fumaric acid, which produces coloured iron salt.



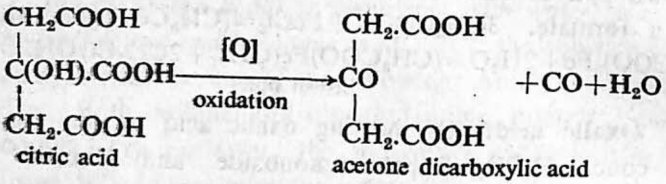
$$\begin{matrix} CHOHCOOH \\ | \\ CHOHCOOH \end{matrix} + O \longrightarrow \underset{\text{dihydroxy fumaric acid.}}{\begin{matrix} C(OH)COOH \\ \| \\ C(OH).COOH \end{matrix}}$$

6. Citric acid: *Denige's test.* In presence of an acid solution of mercuric sulphate potassium permanganate gives with citric acid or a citrate a heavy white ppt. having the composition.

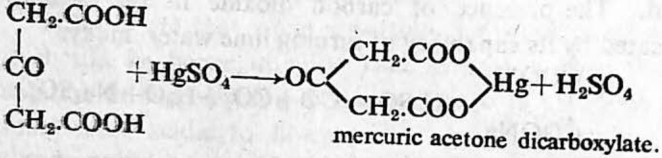


$$SO_4\left\langle\begin{matrix}HgO\\HgO\end{matrix}\right\rangle Hg\left(2CO\left\langle\begin{matrix}CH_2.COO\\CH_2.COO\end{matrix}\right\rangle Hg\right)$$

The ppt. is a double salt of basic mercuric sulphate with mercuric acetone dicarboxylate.



$$\underset{\text{citric acid}}{\begin{matrix}CH_2COOH\\|\\C(OH).COOH\\|\\CH_2.COOH\end{matrix}}\xrightarrow[\text{oxidation}]{[O]}\underset{\text{acetone dicarboxylic acid}}{\begin{matrix}CH_2.COOH\\|\\CO\\|\\CH_2.COOH\end{matrix}}+CO+H_2O$$



$$\begin{matrix}CH_2.COOH\\|\\CO\\|\\CH_2.COOH\end{matrix}+HgSO_4\longrightarrow\underset{\text{mercuric acetone dicarboxylate.}}{OC\left\langle\begin{matrix}CH_2.COO\\CH_2.COO\end{matrix}\right\rangle Hg}+H_2SO_4$$

7. Benzoic acid: (*a*) When heated with *sodalime* benzoic acid or a benzoate yields benzene.

$$C_6H_5COONa+NaOH=C_6H_6+Na_2CO_3.$$

(*b*) With a neutral solution of benzoate, ferric chloride solution produces a buff-coloured ppt. of basic ferric benzoate, which dissolves in dil. HCl giving a white crystalline ppt. of benzoic acid.

$$3C_6H_5COONa+2FeCl_3+3H_2O$$
$$=(C_6H_5COO)_3Fe.Fe(OH)_3+3HCl+3NaCl$$
$$(C_6H_5COO)_3Fe.Fe(OH)_3+6HCl$$
$$=3C_6H_5COOH+2FeCl_3+3H_2O.$$

8. Salicylic acid: (*a*) $\underset{\text{salicylic acid}}{C_6H_4(OH)COOH}\xrightarrow{\text{heat}}\underset{\text{phenol}}{C_6H_5OH}+CO_2$

(*b*) A salicylate + sodalime $\xrightarrow{\text{heat}}$ Phenol + Na_2CO_3.

$$C_6H_4(OH)COONa+NaOH\xrightarrow{\text{heat}}C_6H_5OH+Na_2CO_3$$

(*c*) *Oil of wintergreen test.* When salicylic acid or a salicylate is heated with conc. H_2SO_4 and methyl alcohol, methyl salicylate is formed.

$$C_6H_4(OH)COOH+CH_3OH+H_2SO_4 \longrightarrow C_6H_4(OH)COOCH_3 + [H_2O+H_2SO_4]$$

9. Methyl alcohol : (*a*) *Copper coil oxidation.* Methyl alcohol is oxidised to formaldehyde.

$$2CH_3OH+O_2=2CH_2O+2H_2O.$$

(*b*) *Oil of wintergreen test.* Methyl salicylate is formed (*see* above for reaction).

10. Ethyl alcohol: (*a*) *Copper coil oxidation.* Ethyl alcohol is oxidised to acetaldehyde.

$$CH_3CH_2OH \xrightarrow{O} CH_3CHO.$$

(*b*) *Iodoform reaction*

$$C_2H_5OH+6NaOH+4I_2=CHI_3+5NaI+5H_2O+HCOONa$$

11. Acetone: (*a*) *Iodoform reaction.*

$$CH_3COCH_3+4NaOH+3I_2 = CHI_3+CH_3COONa+3NaI+3H_2O.$$

(*b*) *Denige's test.* The ppt. that is obtained is a double compound of acetone with basic mercuric sulphate.

$$2HgSO_4.3HgO.CO(CH_3)_2.$$

12. Benzaldehyde: On reaction with a strong solution of caustic alkali benzaldehyde is converted into benzyl alcohol and the alkali salt of benzoic acid.

$$\underset{\text{benzaldehyde}}{2C_6H_5CHO}+NaOH=\underset{\text{benzyl alcohol}}{C_6H_5CH_2OH}+\underset{\text{sodium benzoate}}{C_6H_5COONa}$$

13. Glycerine: (*a*) *Acrolein test.* Glycerine on being heated with potassium hydrogen sulphate is coverted into acrolein.

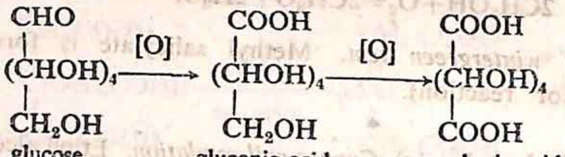
$$\underset{\text{glycerine}}{CH_2OHCHOHCH_2OH} \xrightarrow{-2H_2O} \underset{\text{acrolein}}{CH_2=CHCHO}$$

(*b*) *Dunstan's test.* Borax in solution gets hydrolysed to boric acid and caustic soda and hence the solution reacts alkaline.

$$Na_2B_4O_7+7H_2O \rightleftharpoons 2NaOH+4H_3BO_3$$

Glycerine, a hydroxy compound combines with boric acid to form a complex, which is much stronger than boric acid and hence the solution no longer reacts alkaline to phenolphthalein.

14. Glucose: Its *reducing action* is because of the following reaction:



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{[O]} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{[O]} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}$$

glucose gluconic acid saccharic acid

15. Cane-sugar: Cane-sugar solution, if boiled with dilute sulphuric acid or dilute hydrochloric acid undergoes *hydrolysis* to glucose and fructose.

$$\underset{\text{cane-sugar}}{C_{12}H_{22}O_{11}}+H_2O=\underset{\text{glucose}}{C_6H_{12}O_6}+\underset{\text{fructose}}{C_6H_{12}O_6}$$

16. Starch: On boiling with dil. HCl or dil H_2SO_4 starch is *hydrolysed* into dextrose (glucose).

$$\underset{\text{starch}}{(C_6H_{10}O_5)n}+nH_2O=\underset{\text{dextrose}}{n(C_6H_{12}O_6)}.$$

17. Chloroform: *Carbylamine reaction.* See page 128.

18. Aniline: (*a*) *Carbylamine reaction.* see page 128.
(*b*) *Diazo reaction.* See page 129.

19. Dimethylaniline: (*a*) *Formation of an azo colour.*

Aniline on diazotisation is converted into benzene diazonium chloride, which, on subsequent reaction with dimethylaniline produces dimethyl aminoazobenzene hydrochloride.

$$C_6H_5N=NCl+C_6H_5N(CH_3)_2 \longrightarrow C_6H_5N=NC_6H_4N(CH_3)_2HCl.$$

(*b*) *Formation of p-nitrosodimethylaniline.*

$$C_6H_5N(CH_3)_2HCl+NaNO_2+HCl \longrightarrow O=N\text{-}C_6H_4N(CH_3)_2HCl+NaCl+H_2O.$$

p-nitrosodimethylanilinehydrochloride.

On being rendered alkaline the solution or the ppt. as the case may be turns green because of liberation of the free base.

$$O{=}N\text{-}C_6H_4N(CH_3)_2HCl+NaOH \xrightarrow{\quad} O{=}NC_6H_4N(CH_3)_2+NaCl+H_2O.$$

20. Nitrobenzene: *Reduction and diazo reaction.*

Reduction: $R-NO_2+6H=RNH_2+2H_2O$.

For diazo-reaction *see* page 129.

21. Urea: (*a*) *Reaction with nitrous acid.* When urea reacts with sodium nitrite and hydrochloric acid (*i.e.*, nitrous acid), carbon dioxide, nitrogen and water are formed.

$$NH_2CONH_2+2HONO=CO_2+2N_2+3H_2O.$$

(*b*) *Biuret reaction.* When gently heated, urea melts and suddenly solidifies to a colourless crystalline solid called biuret and ammonia is simultaneously evolved.

$$\underset{\text{urea}}{NH_2CONH}\,\boxed{H+H_2N}\,\underset{\text{urea}}{CO.NH_2}\longrightarrow\underset{\text{biuret}}{NH_2CONHCONH_2}+NH_3$$

Specimen Records of Analytical Results

Sample No........

Date......

The given sample is a colourless liquid having an alcoholic odour.

Experiments	Observations	Inferences
1. A portion of the sample was shaken with a little water in a test-tube and the resulting mixture was tested with litmus paper.	The substance dissolved and the resulting solution had no action on litmus paper.	Water soluble neutral substance.
2. A portion of the sample was evaporated to dryness.	No residue	Methyl alcohol, ethyl alcohol. acetone.
3. To a little of the aqueous solution of the sample in a test-tube an equal volume of a concentrated solution of iodine in potassium iodide was added. After warming a little a dil. solution of caustic soda was added dropwise till the brown colour due to iodine vanished. The test-tube was then finally cooled.	A yellow crystalline ppt. of iodoform with a peculiar but characteristic odour came down.	Acetone, ethyl alcohol
4. The same reaction as outlined in (3) above was repeated in presence of NH_4OH instead of NaOH.	No iodoform (*i.e.*, no ppt., no odour).	Acetone absent.
5. A portion of the sample was oxidised by copper coil and the oxidised liquid was divided into *three* parts :		
(*a*) To one part a few drops of freshly prepared Schiff's reagent was added.	Pink colour deepening gradually	Ethyl alcohol
(*b*) To another part a dil. solution of sodium nitroprusside followed by a few drops of dil. NaOH solution was added.	Production of Wine-red colour	Ethyl alcohol

Experiment	Observation	Inference
(c) From the remaining portion of the oxidised liquid 1 c.c. was taken and then an equal volume of a freshly prepared dil. solution of sodium nitroprusside was added to it. Finally a drop of piperidine was added.	Development of a deep blue colour.	Ethyl alcohol

The given sample is therefore *ethyl alcohol.*

Sample No........

Date.....

The given sample is a white crystalline solid.

Experiments	Observations	Inferences
1. A portion of the sample was shaken with water in a test-tube and the resulting mixture was tested with litmus paper.	The substance dissolved and the resulting solution had no action on litmus paper.	Water soluble neutral substance.
2. A little of the solid was heated in a hard glass test-tube.	Charring with the smell of burnt sugar.	Carbohydrates
3. A portion of the sample was shaken with dil. NaOH solution.	The solution turning yellow on heating.	Carbohydrates
4. A little of the sample was warmed with conc. H_2SO_4	Immediate blackening with evolution of gases.	Sugars, Tartrate, Starch
5. To about 1 c.c. of the aqueous solution of the sample 2 drops of a 15% solution of α-naphthol was added. Now carefully and without shaking 2 c.c. of conc. H_2SO_4 was added down the side of the test-tube.	A violet colour at the junction of two liquid layers.	Carbohydrates

Experiments	Observations	Inferences
6. To a little of the aqueous solution of the sample a drop of a dil. solution of iodine in potassium iodide was added.	No change	Starch absent
7. To 1 c.c. of the aqueous solution 1 c.c. of Fehling's solution was added and the mixture subsequently heated.	A yellow ppt. gradually turning red.	Glucose or lactose.
8. To 1 c.c. of the aqueous solution of the sample 2 c.c. of Barfoed's reagent was added and after thorough mixing the test-tube was placed in water kept boiling in a beaker.	A red ppt.	Glucose
9. To about 10 c.c. of a dilute aqueous solution of the sample a solution containing phenylhydrazine hydrochloride (or sulphate) and NaAc was added. The mixture was then warmed by placing the test-tube in water kept boiling in a beaker.	A yellow mass crystallising out of hot solution.	Glucose

The given sample is therefore *Glucose.*

Sample No......

Date......

The given sample is a white crystalline solid, fluffy in appearance.

Experiments	Observations	Inferences
1. A portion of the sample was shaken with water in a test-tube and the resulting mixture was tested with litmus paper.	The sample dissolved partly in the cold and the resulting mixture reacted acidic to litmus.	Acidic substance sparingly soluble in cold water but readily in hot water.
The above mixture was then heated.	The substance readily dissolved.	

Experiments	Observations	Inferences
2. To a suspension of the sample in water solid bicarbonate was added little by little.	Effervescence occurred and the substance dissolved.	Benzoic, salicylic and succinic acid.
3. A portion of the sample was heated in a hard glass test-tube.	Melting followed by sublimation with evolution of odour of phenol.	Probably salicylic acid
4. A portion of the solid was warmed with conc. H_2SO_4.	Slow blackening with evolution of gases.	May be salicylic acid.
5. A little of the sample was heated with sodalime.	Odour of phenol.	Salicylic acid

A neutral solution of the sample was then prepared by adding powdered sodium carbonate to a suspension of the sample in water. With the neutral solution thus obtained, the following *wet reactions* 1, 2, 3, 4 were carried out taking a little portion of it each time.

Experiments	Observations	Inferences
1. To a portion of the neutral solution dil. H_2SO_4 was added.	A white crystalline ppt., soluble on boiling but reappeared on cooling.	Benzoic or salicylic acid.
2. To a portion of the solution freshly prepared neutral ferric chloride solution was added.	Violet colour, not discharged by acetic acid.	Salicylic acid and not benzoic acid
3. To a portion of the neutral solution an equal volume of $CaCl_2$ solution was added.	No change	— —

Experiments	Observations	Inferences
4. An excess of bromine water was added to a portion of the neutral solution of the sample.	A pale yellow ppt.	Salicylic acid
5. 0·1g of the sample was mixed with 1 c.c. of a mixture of MeOH and conc. H_2SO_4 and was then heated for about 3-4 minutes. It was cooled and then poured into a little solution of Na_2CO_3 contained in a basin.	A characteristic fragrant odour.	Salicylic acid

Hence, the supplied sample is *salicylic acid.*

CHAPTER III

IDENTIFICATION OF AN ORGANIC SAMPLE GIVEN SINGLY IN PURE CONDITION

Detection of an organic sample containing one of the commonly known organic compounds becomes much easy, when it is supplied in *pure* condition.

Below is given the list of commonly known organic compounds from which one may be supplied in a state of purity for identification:

(*a*) Methyl alcohol, (*b*) Ethyl alcohol, (*c*) Acetone, (*d*) Aniline, (*e*) Dimethylaniline, (*f*) Acetic acid, (*g*) Formic acid, (*h*) Benzoic acid, (*i*) Salicylic acid, (*j*) Oxalic acid, (*k*) Citric acid, (*l*) Tartaric acid, (*m*) Succinic acid, (*n*) Cane-sugar, (*o*) Glucose, (*p*) Lactose, (*q*) Starch, (*r*) Chloroform, (*s*) Benzene, (*t*) Phenol, (*u*) Glycerol, (*v*) Benzaldehyde, (*w*) Nitrobenzene, (*x*) Resorcinol, (*y*) Betanaphthol, (*z*) Urea.

In such a case proceed as follows:

1. (*a*) After noting the state of aggregation, colour and odour of the sample, shake a portion of it with a little water in a test-tube and test the resulting aqueous solution or suspension with litmus paper.

(*b*) If sparingly soluble in cold water, heat the mixture.

(A) (*i*) Sample is a *colourless* (or white), *odourless solid* and reacts *acidic* to litmus: Resorcinol†, oxalic, succinic, tartaric, citric, benzoic and salicylic acids. Test with $NaHCO_3$ to distinguish resorcinol from acids. Resorcinol gives no effervescence, while an acid does. If resorcinol is indicated, carry out the reaction as detailed under resorcinol (p 148).

If moderately or highly soluble in cold water, one of the first five and if sparingly soluble in cold but readily in hot water, either of the last two compounds (benzoic & salicylic) is indicated.

(*ii*) But if the *solid* possesses a *phenolic odour*, reacts *acidic* to litmus and is not much soluble in water, phenol* is indicated. Test with $NaHCO_3$ to distinguish phenol from acids (page 199).

(B) (*i*) Sample is a *liquid* having a pungent or characteristic vinegar *odour*, reacts *acidic* to litmus and miscible with water in all proportions: Formic or acetic acid.

(*ii*) But if the *liquid* possesses a characteritic *carbolic* (phenolic) *odour*, reacts *acidic* to litmus and is not much soluble in water, phenol* is indicated.

---

† Odinarily resorcinol is gray in colour because of atmospheric oxidation.

*Phenol is weakly acidic and at 65·3° or higher temperature miscible with water in all proportions.

(C) Sample is a *solid* and is *without any action* on litmus: Cane-sugar, glucose, lactose, starch, betanaphthol and urea. Of which only startch* and betanaphthol are insoluble in water and the latter possesses a faint characteristic phenolic odour.

(D) Sample is a *liquid* and is *without any action* on litmus: Methyl alcohol, ethyl alcohol, acetone, glycerol, chloroform, benzene, benzaldehyde, nitrobenzene, aniline & dimethylaniline. All save and except glycerol possess a characteristic odour. All are colourless; exception nitrobenzene, which has a pale yellow colour.

If miscible with water in all proportions, one of the first four liquids is indicated. If not, one of the remaining liquids is indicated.

(A) Distinguishing solid acids.

Expt. I. Heat a little of the given solid in a hard glass test-tube.

Observations	Inferences
(*a*) *No charring*, but gives off	
(*i*) Irritating fumes	Succinic acid
(*ii*) irritating fumes having aromatic odour	Benzoic acid
(*iii*) phenolic odour	Salicylic acid
(*b*) *Charring occurs* with the evolution of	
(*i*) smell of burnt sugar	Tartaric acid
(*ii*) acrid vapours	Citric acid

Expt. II. Heat a little of the solid with conc. H_2SO_4

Observations	Inferences
(*a*) *Immediate blackening occurs* and the substance gives off gases.	Tartaric acid
(*b*) *No immediate blackening*, which occurs only slowly with the evolution of gases.	Citric & salicylic acids.
(*c*) *No blackening at all*:	
(*i*) The evolved gas when passed through lime water, the latter turns milky.	Oxalic acid
(*ii*) Acid fumes having irritating aromatic odour.	Benzoic acid

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*There is a variety, which gives a clear solution on boiling with water.

Expt. III. Mix the solid with 3-4 times of its weight of dry sodalime and heat the resulting mixture strongly in a hard glass test-tube.

Observations	Inferences
(*i*) Odour of benzene, the evolved vapours burn with a smoky flame.	Benzoic acid
(*ii*) Odour of phenol is evolved	Salicylic acid

Wet reactions

Unless otherwise stated carry out the wet reactions with the neutralised (*see* page 135 along with the foot note given there) solution.

Expt. I. To a little of the solution taken in a test-tube add a drop or two of a freshly prepared neutral ferric chloride solution and note immediately the change of colour that might have taken place.

Observations	Inferences
(*i*) Violet colour is developed, which is not discharged by acetic acid.	Salicylic acid
(*ii*) A buff-coloured precipitate—	
(*a*) buff colour disappears and instead a white crystalline ppt. appears	Benzoic acid
(*b*) buff-colour disappears but no white ppt. appears	Succinic acid
on acidifying with dil. HCl.	

Expt. II. To a portion of the neutral solution add an equal volume of calcium chloride solution.

Observations	Inferences
(*i*) An immediate white ppt. which does not dissolve in acetic acid, but dissolves in dil. HCl or dil. HNO_3.	Oxalic acid
(*ii*) A sand-like ppt. on shaking and scratching the inside of the test-tube.	Tartaric and Succinic acids
(*iii*) No ppt. even on shaking and scratching but on boiling only.	Citric acid

Expt. III. Add an equal volume of Denige's reagent to a little portion of the original solution in the cold.

Observations	Inferences
(*a*) An immediate white ppt., which does not dissolve on boiling.	Oxalic acid
(*b*) No precipitation in the cold and even on boiling the mixture, but	
a white ppt. or turbidity appears on adding to the hot mixture a drop or two of a 2% solution of $KMnO_4$, the colour of which is discharged.	Citric acid

The next step here is to *confirm* or recognise the suspected acid by carrying out individual characteristic reactions. But oxalic, citric & benzoic acids, it should be noted, if supplied for identification, require no additional test; the reactions stated earlier will stand as a sufficient proof for their presence.

(*i*) If succinic acid be suspected, perform the *Fluorescein test* (page 140) to confirm your findings.

(*ii*) If tartaric acid be indicated, try the *Mirror test* and *Fenton's test* (page 142) to confirm their presence.

(*iii*) When salicylic acid is indicated (α) carry out the reaction with bromine water (page 146; expt.-VI) and then confirm (β) by carrying out *oil of wintergreen test* (page 146; expt.-IV) with 0·1 gm. of the solid.

(*iv*) Further evidence for benzoic acid, if necessary, may be adduced by carrying out expt.-VII described in page 145.

(B) Distinguishing liquids reacting acidic to litmus

Three substances come under this heading: Formic acid, acetic acid and phenol.

Expt. I. Evaporate a portion of the sample to dryness by careful heating in a clean basin (in its absence a test-tube) over a small flame.

Observations	Inferences
The substance completely volatilises away. The evolved vapour gives off:	
(*a*) Pungent smell	(*a*) Formic acid
(*b*) Vinegar odour	(*b*) Acetic acid
(*c*) Carbolic odour	(*c*) Phenol*

Expt. II. Add a little of the sample to a solution of $NaHCO_3$ taken in a test-tube.

Observations	Inferences
(*a*) Effervescence occurs	Formic aoid, acetic acid.
(*b*) No effervescence	Phenol

After completion of the above experiments carry out the following *wet reactions* with the neutralised (*see* page 135) solution of the sample.

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*Phenol may leave a reddish syrupy residue on evaporation; but pure phenol volatilises away completely on strong heating.

Expt. I. To a little of the solution taken in a test-tube add a drop or two of a freshly prepared neutral ferric chloride solution and note immediately the change of colour that might have taken place.

Observations	Inferences
(*a*) Red colour is developed.	Formic acid, acetic acid.
(*b*) Violet colour is developed, & the colour is discharged on addition of acetic acid.	Phenol

Confirmatory reactions

Now according to the demand of the situation carry out the reactions [either (*i*) (α) & (β) or (*ii*) (α) & (β)] described in page 179 to confirm your findings.

(C) Distinguishing solids having no action on litmus

Expt. I. Shake a portion of the substance with a little of dil. solution of caustic soda and finally heat slightly.

Observations	Inferences
(*a*) Brown resinous mass	Carbohydrates
(*b*) The substance dissolves—	Water soluble substances & betanaphthol.
(*i*) If insoluble in water but dissolves in caustic soda;	Betanaphthol
(*ii*) pungent smell of ammonia	Urea

Expt. II. Heat a little of the solid in a test-tube.

Observations	Inferences
(*a*) *Charring occurs* with the evolution of:	
(*i*) Smell of burnt sugar	Sugars (glucose, sucrose, lactose)
(*ii*) Smell of burnt wood or leather	Starch
(*b*) *No charring*, but gives off odour of:	
(*i*) Ammonia	Urea

Expt. III. Warm a little of the solid with conc. H_2SO_4 in a test-tube.

Observation	Inference
Immediate blackening occurs and the substance gives off gases.	Sugars, starch

After the completion of the above experiments carry out the following *wet reactions* with the sample.

Expt. I. *Ferric chloride test* [page 118, expts. (*e*) & (*f*)]

Observation	Inference
A green coloration and afterwards a flocculant ppt.	Betanaphthol

Expt. II. *Molisch's test* (indicated under glucose in page 158).

Observation	Inference
A blue or violet colour at the junction of two liquid layers.	Carbohydrates

Now carry out one or more of the following experiments as may be necessary to *confirm* the substance already suspected.

If betanaphthol is indicated, adduce further evidence by carrying out the expt.-(IV), (V) & (VI) described under betanaphthol in page 149.

When urea is indicated, confirm by *Biuret reaction* [expt-(II)] and by expts.-(IV) & (V) described in page 165.

If the Molisch's test is positive, try the reactions according to direction given in pages 180–181 under item viii (*i.e.*, examination of carbohydrates).

(D) Distinguishing liquids having no action on litmus

The compounds that come under this class are divided, as have already been stated, into two groups depending upon their miscibility with water.

Miscible with water in all proportions: Methyl alcohol, ethyl alcohol, acetone and glycerol.

Immiscible with water: Chloroform[1], benzene[1], benzaldehyde, nitrobenzene[2], aniline[3] and dimethylaniline[3].

Expt. I. Evaporate a portion of the sample to dryness by careful heating in a clean basin (in its absence a test-tube) over a small flame.

Observations	Inferences
(*a*) Syrupy residue	Glycerol*
(*b*) No residue	One of all the liquids mentioned above.

Of the *water-miscible liquids* indicated, glycerol is an odourless, syrupy liquid. Confirm glycerol, if suspected, by *acrolein test* and *Dunstan's test* described in page 154. The other three liquids have characteristic odour. Alcholic smell indicates either of the alcohols, whereas acetone possesses a characteristic pleasant odour. Hence when the sample has an odour perform the experiments according to the direction under item (*ia*) and (*iβ*) in page 182.

Of the *water-immiscible liquids* aniline and dimethylaniline are soluble in dil. HCl. Hence if the sample dissolves in dil. HCl on shaking and warming, it must be either of the two. Besides, both of them possess characteristic odour. Try, however the individual characteristic reactions: *Diazo reaction* (page 124) for aniline and formation of *azo-colour*, *p-nitrosodimethylhylaniline* and *malachite green* (page 164, 155) for dimethylaniline.

For the remaining four liquids proceed according to the directions given in the third paragraph (page 183) and carry out one or more reactions [described under items (*i*), (*ii*), (*iii*)-(*a*) & (*b*) in pages 183–184] as may be necessary to recognise the substance.

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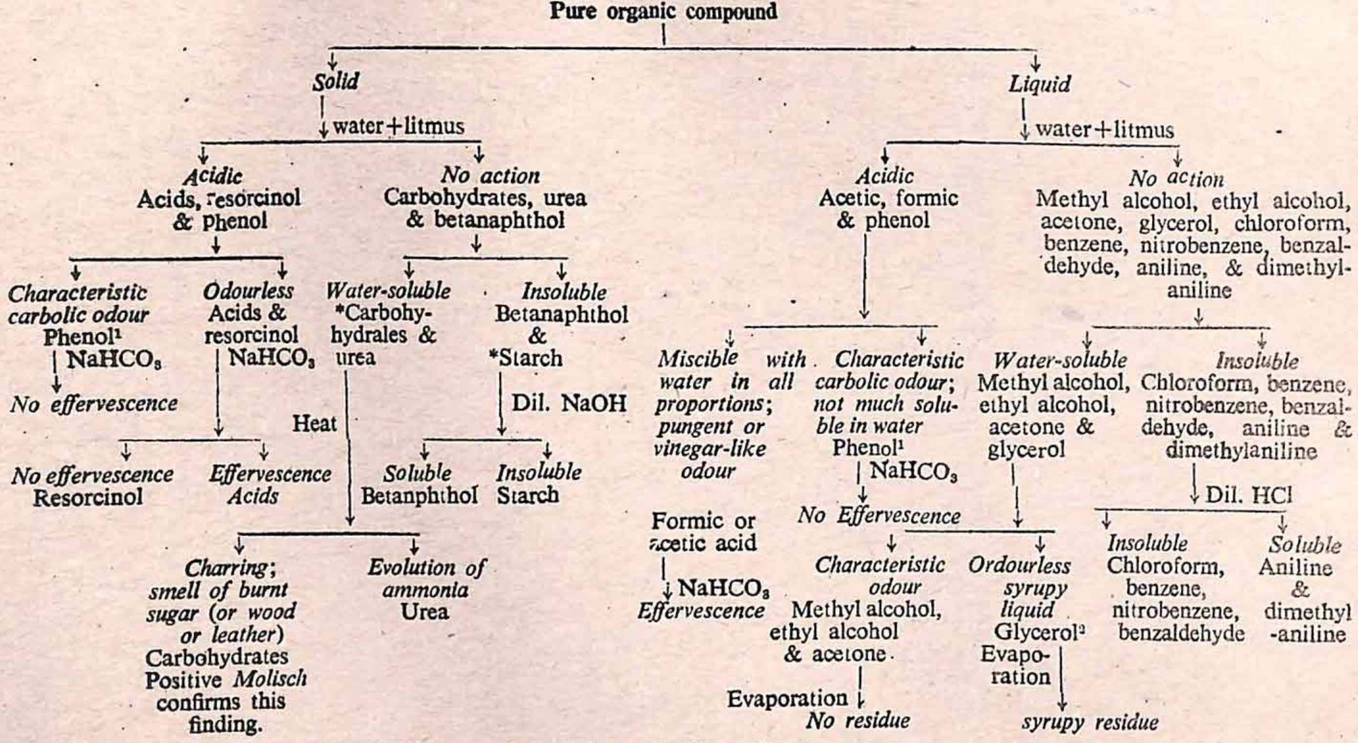
*Glycerol may sometimes evaporate away leaving no residue but a faint stain.

[1] Highly volatile.

[2] Insoluble in dilute acid and alkali.

[3] Soluble in dil. acid but insoluble in alkali.

To obviate the difficulties of beginners a table, which is a brief outline of the scheme already detailed is furnished below:


Pure organic compound
Solid
water + litmus
Acidic
Acids, resorcinol & phenol
No action
Carbohydrates, urea & betanaphthol
Characteristic carbolic odour
Phenol[1]
NaHCO₃
No effervescence
Odourless
Acids & resorcinol
NaHCO₃
No effervescence
Resorcinol
Effervescence
Acids
Water-soluble
*Carbohydrales & urea
Heat
Charring; smell of burnt sugar (or wood or leather)
Carbohydrates
Positive Molisch confirms this finding.
Evolution of ammonia
Urea
Insoluble
Betanaphthol & *Starch
Dil. NaOH
Soluble
Betanphthol
Insoluble
Starch
Liquid
water + litmus
Acidic
Acetic, formic & phenol
Miscible with water in all proportions; pungent or vinegar-like odour
Formic or acetic acid
NaHCO₃
Effervescence
Characteristic carbolic odour; not much soluble in water
Phenol[1]
NaHCO₃
No Effervescence
No action
Methyl alcohol, ethyl alcohol, acetone, glycerol, chloroform, benzene, nitrobenzene, benzaldehyde, aniline, & dimethylaniline
Water-soluble
Methyl alcohol, ethyl alcohol, acetone & glycerol
Characteristic odour
Methyl alcohol, ethyl alcohol & acetone
Evaporation
No residue
Ordourless syrupy liquid
Glycerol[2]
Evaporation
syrupy residue
Insoluble
Chloroform, benzene, nitrobenzene, benzaldehyde, aniline & dimethylaniline
Dil. HCl
Insoluble
Chloroform, benzene, nitrobenzene, benzaldehyde
Soluble
Aniline & dimethyl-aniline

---

*There is a variety of starch, which gives a clear solution on boiling with water.

[1] At 65.3; or higher temperature, it is miscible with water in all proportions.

[2] Glycerol may sometimes evaporate away leaving no residue but a faint stain only.

PART III

QUANTITATIVE ANALYSIS

CHAPTER I

GENERAL CONSIDERATION

Quantitative analysis, *i.e.*, the determination of the amount of an element or radical present in the sample is a very important part of analytical chemistry and this is, as per direction of the syllabi, done either by **Volumetric** or by **Gravimetric** processes though other methods are there. Neatness, accuracy in weighing and in measurements of volumes, careful handling of the experimental solution (so that no part of the solution is lost) at all stages of operation and careful handling of the apparatus can only give correct results.

In volumetric analysis the sample supplied is allowed to react with a suitable reagent of known concentration, under such a condition as the reaction goes to completion. The end-point of the reaction is to be sharp so that it can be noted either directly or with the help of an indicator. Knowing the volume of the standard solution (*i.e.*, the reagent of known concentration), that reacts with a definite volume of the experimental solution, the amount of the substance to be determined is calculated with the help of laws of chemical equivalence. In gravimetric analysis the element or radical to be determined is generally isolated from a known volume of the solution in the form of a pure, stable and usually insoluble compound by the addition of suitable reagents under appropriate conditions. This insoluble compound is weighed as such, if possible or converted into a form suitable for weighing. Then from the knowledge of the molecular weight of the compound and the atomic weights of the constituent elements, the amount of the element or radical present in the sample is calculated.

Use of balance: Both the volumetric and the gravimetric processes require a sensitive and accurate chemical balance. With the help of such a balance weights accurate up to the tenth of a milligram (0·0001 gm.) can be known. There are two horizontal scales in a balance, one at the top and the other at the base. The scale at the top is called the *rider scale* whilst the scale at the bottom is called the *pointer scale*. A rider is a thin metal wire (weighing 0·005 g. in the case of Bunge and 0·01 g, in the case of Sartorius) bent in such a way that it can be placed anywhere on the rider scale so that weight adjustment up to 10 mg. can be made.

In Bunge balance the rider is placed at the extreme left corner of the balance beam. This extreme position is marked zero. The rider scale is divided into ten big eqaual divisions, each of this big division is again divided into ten equal divisions. Then from zero to extreme right position, which is marked 10 there are 100 teeth. The shifting of rider from zero to ten is the same as to add 0·01 gm. on the right pan. Therefore shifting of rider by one tooth is equivalent to $\frac{0{\cdot}01}{100}$ gm. or, 0·0001 gm.

In Sartorius balance zero is at the middle of the rider scale. On each side of the zero mark there are ten large divisions. Each of this division in its turn is divided into five small divisions. Thus shifting of rider from zero to ten means passing over a range of 50 teeth, which corresponds to 0·01 gm. weight. Hence shifting of rider by one tooth is equivalent to $\frac{0{\cdot}01}{50}$ gm. or 0·0002 gm. The knowledge of the value of one division of the rider scale is essential in accurate weighing. Placing the rider on the left side of 'zero' means a decrease of weight on the right pan, whilst that to the right of 'zero' means an increase of weight on the same.

Weighing by difference: Before entering into actual weighing see: (*i*) that the pointer moves equal no. of divisions on either side of midline of the pointer scale; (*ii*) that all the weights are there in the weight box and these weights are placed in their proper places. These being done take some quantity of the finely powdered substance to be weighed in a glass-stoppered. perfectly cleaned weighing bottle and place it on the left pan.

Place the highest weight on the right-hand pan and set the beam free to swing by releasing the rest-knob and note the displacement of the pointer. If the pointer moves to the left of the midline of pointer scale, the weight on the right-hand pan is comparatively heavy. Bring the balance at rest and replace the weight by next smaller one. Set the balance again free to swing as before; if the pointer moves to the right of the midline, the weight on the right-hand pan is little too small. Don't remove the weight placed on the right-hand pan; add on the next smaller one. Try with all the successive weights of the weight box in this way without omitting any till the 10 mg. weight has been tried by placing it on the right-hand pan. If the weights placed be little higher (indicated by the movement of the pointer), remove the 10 mg. weight and use the rider for adding still smaller weights. But if the weights placed be little smaller (indicated by the movement of the pointer to the right) retain all the weights and use rider for adding still smaller weights. Note down the weights from the blank spaces in the weight box and check them while removing the weights from scale pan back to the box. Never place the weights anywhere other than the scale pan or in its place in the weight box. Read the position of the rider and add the appropriate value (according as the balance used is Bunge or Sartorius) to the weights already noted. Suppose this weight (*i.e.*, the weight of the weighing bottle with its contents) is 18·9761 gms. and you want to take out about 1·5182 gms. of its contents. Remove the weights equivalent to 1·5 gms. from the right-hand pan. Note the oscillation of the pointer—it moves to the right, pointing out that the weighing bottle is heavier. Take out the weighing bottle, hold it over a clean funnel fitted on to a clean measuring flask (the volume of the measuring flask is dependent on the strength of the solution to be prepared) or any other suitable vessel and tap out a little of the substance on the funnel, opening the stopper of the bottle. While tapping out the substance take care so that no particle is transferred outside the funnel and the flask. Put the stoppered bottle again on the left pan, set the balance swinging. Note the oscillation of the pointer. If it still moves to the right, repeat the process of pouring out the substance, noting the oscillation of the pointer till it moves to the left. The weighing bottle is now lighter than the weights placed on the right-hand pan, *i.e.*, more than 1·5 gms. of the substance have been transferred out. Place the bottle again on the left pan, remove all the weights from the right-hand pan and bring the rider back to zero mark of the rider scale. Now exactly counterpoise the weighing bottle in a manner similar to before. Note the weights. The difference between the 1st. weight and this final weight gives the weight of the sample taken into the funnel and the flask. Let this final weight be 17·4367 gms. Hence the weight of the substance transferred=(18·9761—17·4367) gms.=1·5394 gms. Now place the weights in their proper places in the box and bring the rider to zero mark.

N.B. The balance must be brought at rest, while

(*i*) placing on or removing weights from the pan;
(*ii*) shifting the rider along the scale;
(*iii*) placing on or removing the weighing bottle from the pan;
(*iv*) leaving the balance after completion of the work.

Note also that during weighing, while the balance oscillates, the glass windows of the balance must be kept closed, as any air current will cause the pans swing erratically.

For the determination of the weight of a particular substance *see* the chapter on *Gravimetric Processes*.

Preparation of the solution with the substance thus weighed above.

Pour a little distilled water on the funnel so that the substance adhering to the funnel is washed down into the flask. Raise the funnel and rinse it 3 or 4 times using little quantity of distilled water every time and taking care that the stem of the funnel is always inside the flask. Remove the funnel and give the flask a rotatory motion carefully and see that all the solid has undergone solution. (If a clear solution is not obtained by this operation, add more water and again rotate the flask carefully by holding it firmly). Now add distilled water to make the volume of the solution up to the mark (*i.e.*, lower meniscus of the solution just coincides with the mark on the flask). Fit in the stopper, shake the flask, turn it up and down for several times and preserve.

CHAPTER II

VOLUMETRIC ANALYSIS
PRINCIPLE—GENERAL INSTRUCTIONS—STANDARD SOLUTIONS

In volumetric analysis, we have seen that a standard solution is always required. A standard solution is defined as the solution, which contains a known weight of the solute in a definite volume of the solution. Concentration or strength is generally expressed in terms of normality and a solution is said to be a normal one, when it contains one gram-equivalent of the solute per litre of the solution. The equivalent weight expressed in gms. is called gm.-equivalent. Note that the gm.-equivalent is not invariant as the gm.-molecular weight is but depends upon the reaction concerned. The gm.-equivalent of a substance is that weight of it in gms., which in its reaction corresponds to a gm.-atom of hydrogen or a gm.-atom of univalent ion.

Important principles in volumetric analysis

(*a*) As has already been stated that a normal solution contains one gm.-equivalent of solute per litre of the solution. A five normal solution contains 5 times the equivalent weight of the substance in one litre solution of it. Therefore 1 ml. of 5 (N) solution$\equiv$5 ml. of normal (N) solution. A decinormal solution contains 0·1 gm.-equivalent (one-tenth of the equivalent weight) of the solute in one litre solution of it and so on. Hence 1 ml. of 0·1 (N) solution$\equiv$0·1 ml. of (N) solution. In general, if the volume be increased the strength must be decreased proportionately and *vice versa*. This can also be expressed in the following way: Y ml. of a $x(N)$ solution$\equiv$ xY ml. of (N) solution.

(*b*) Normalities being the same, equal volumes of different solutions are chemically equivalent. When one solution is titrated against another, the product of the volume and the strength (in normality) of the unknown solution is equal to the product of the volume (at the equivalence point) and strength (in normality) of the standard solution. Thus, if with V_1 ml. of one solution of strength S_1, V_2 ml. of the other solution of strength S_2 be required for the equivalence point to be reached, then $V_1S_1=V_2S_2$. Hence, strength and volume of one being known the strength of the other can be calculated by knowing the volume which reacted.

(*c*) Normality is the number of gm. equivalent of a solute present in one litre of its solution.

$$\text{Normality}=\frac{\textit{weight of solute in grams per litre}}{\textit{gram-equivalent}}$$

Weight of solute in grams per litre.

$$=\text{Normality}\times\text{gram-equivalent.}$$

(*d*) Reduction of strength by proper dilution; a solution of higher concentration (*i.e.*, strength) may be reduced to lower one (of desired strength) by appropriate dilution.

Example :

$$100 \text{ ml. of a solution of strength } 1{\cdot}19\left(\frac{N}{10}\right)$$

$$=(100\times1{\cdot}19) \text{ ml. solution of strength }\left(\frac{N}{10}\right)$$

∴ (119—100) ml. or 19 ml. water are to be added to 100 ml. of solution of $1{\cdot}19\left(\frac{N}{10}\right)$ in order to make it exactly decinormal.

General instructions

1. Examine that the apparatus to be used are perfectly clean.

2. Rinse the burette and pipette 2 or 3 times with the respective solution to be taken inside and throw away the washings. But never wash the reaction vessels (conical flasks or beakers) with the standard or unknown solutions. Wash these with distilled water.

3. Fill the burette with the solution to a little above zero mark and allow the liquid to run out by opening the stop-cock in order to fill the jet. Close the stop-cock, add more solution if necessary and now allow the liquid to run out dropwise by

opening the stop-cock again till the lower meniscus (upper meniscus in the case of coloured liquids like $KMnO_4$ solution) just touches the zero mark of the burette.

4. Fill the pipette with the solution by suction to 1 to 2 cms. above the mark. Close very quickly the upper end of the pipette by means of the tip of index finger. Wipe out the liquid that adheres to the outside of the lower stem with a blotting paper or filter paper. Allow the liquid to run out slowly by relaxing a little the pressure of the finger till the lower meniscus just touches the graduation mark. If any drop adheres to the tip, remove it by touching the tip against any clean glass surface. Deliver the liquid into the receiving vessel. When the continuous flow has ceased, hold the jet in contact with the inside of the receiving vessel for 15 secs. Now remove the receiving vessel but don't try to collect the solution still remaining in the jet by blowing or by any other means. Note that burette is used to deliver variable volumes, while pipette is generally used to deliver a constant volume of solution.

5. While filling the burette and pipette with the solutions, see that no air bubbles are enclosed in the jet.

6. Repeat the experiment, whenever possible, under identical conditions and take the mean of the titre values for your calculations.

7. Use zero mark of the burette for each titration (if possible) and to take burette reading keep your eyes at the same level with the meniscus to avoid parallax error. Besides, while taking the burette reading, hold a piece of white paper behind the meniscus in the burette.

Different classes of volumetric analysis

A. Reactions in which no change of valency of the reacting ions occurs:

(*i*) acidimetry and alkalimetry.

(*ii*) precipitation reactions.

B. Reactions involving change of valency:

Before proceeding with the different types of volumetric analyses let us take up the preparation of some standard solutions.

Preparation of standard solutions

A standard solution is a solution of accurately known concentration.

Some of the standard solutions are prepared by weighing out accurately and dissolving the solute thus weighed in an appropriate solvent and making up the solution to a known volume. Standard solutions of sodium carbonate, oxalic acid, sodium oxalate, potassium dichromate, etc., for example, are prepared in this way. Since these substances of analytical reagent quality are weighed out and the volumes of the solutions prepared are known, the concentrations are accurately known. These are called primary standard solutions as other substances are standardised against them. But there are substances with which this method of preparation of standard solution cannot be adopted for various reasons, such as instability, variable percentage composition, etc. For the preparation of standard solution of such substances as HCl, H_2SO_4, $KMnO_4$ etc., for examples, solutions of desired *approximate* strength or concentration, as it may be called, are prepared first and then the strength is accurately determined by suitable primary standard solutions. These are secondary standard solutions. Concentrated HCl is about 10·5 to 12 N and the strength of conc. H_2SO_4 is about $36N$. Hence the solutions of these acids having desired approximate strength are prepared by proper dilution of the conc. acids. $KMnO_4$ being a solid a solution of desired *approximate* strength is prepared by weighing out an appropriate amount of this substance in a rough balance and then dissolving in a proper volume of water. Below is given the procedure for the preparation of standard solution of $N/10$ order, of accurately known strength.

Standard solution of Na_2CO_3.

Equivalent weight of Na_2CO_3 is 53. Hence in order to prepare 250 ml. $0{\cdot}1N$ solution of sodium carbonate 1·325 gms. of sodium carbonate of analytical reagent quality are required.

Procedure

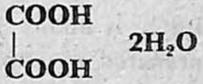
Weigh out accurately about 1·3 gm. of pure sodium carbonate into a clean 250 ml. volumetric flask (*see* the method of weighing, p. 208). Wash down the whole of sodium carbonate by careful addition of distilled water. Shake the flask carefully, holding it firmly. When all the solid has dissolved, make up the volume to the mark (*see* the method of preparation of solution, p. 210).

Let the weight of Na_2CO_3 taken= w gms.

$\therefore$ Strength of prepared Na_2CO_3 solution $= \frac{w}{1{\cdot}325}\,\frac{N}{10}$

[Calculate up to 4th. place of decimal]

Standard solution of oxalic acid



$$\begin{array}{c}COOH\\ |\\ COOH\end{array}\quad 2H_2O$$

Equivalent weight of oxalic acid is 63. Hence in order to prepare 250 ml. of 0·1 N solution of oxalic acid 1·575 gms. are required.

Procedure

Weigh out accurately about 1·5 gms. of analytical reagent quality oxalic acid into a clean 250 ml. volumetric flask (*see* the method. of weighing, p. 208). Wash down the entire quantity of solid into the flask by careful addition of distilled water. Hold the flask firmly and shake carefully. When all the solid has dissolved, make up the volume to the mark (*see* the method of preparation of solution, p. 210).

Let the weight of oxalic acid taken= w gms.

$\therefore$ Strength of oxalic acid solution$= \frac{w}{1{\cdot}575}\,\frac{N}{10}$

[Calculate up to 4th. place of decimal]

Preparation of standard solution of sodium oxalate $Na_2C_2O_4$, *Potassium dichromate* $K_2Cr_2O_7$, *etc., are left out for the present and they will be discussed later on in their proper places.* Let us now confine ourselves to the preparation of some standard solutions, which cannot be taken as primary standard.

Preparation of N/10 HCl

Conc. HCl is about 10·5 to 12N. Acid of desired approximate strength is prepared by appropriate dilution.

Procedure

Measure out about 9 ml. of conc. acid in a measuring cylinder. Take in a litre flask about 500 ml. of distilled water and pour the measured acid into this flask and make up the volume to the mark with distilled water. Shake thoroughly so as to form a uniform solution. The strength of this solution is approximately *N*/10. To find out exact strength titrate it against a standard alkali using a suitable indicator (*see* pp. 218, 220).

Preparation of N/10 H_2SO_4

Conc. H_2SO_4 is about 36*N*. Acid of desired approximate strength is prepared by appropriate dilution.

Procedure

Measure out by means of a measuring cylinder about 2·8 ml. of conc. acid. Pour this acid slowly into a big beaker containing about 500 ml. of distilled water with constant stirring. [Cool, if necessary, while pouring down the acid into the beaker.] Now transfer the solution into a litre bottle and make up the volume with distilled water. The strength of this solution is approximately *N*/10. To find out the exact strength titrate it against a standard alkali using a suitable indicator (*see* pp. 218-220).

N.B. *Always* **add** *acid to water and* **not** *the reverse.*

Preparation of N/10 NaOH

Equivalent weight of NaOH is 40. Hence in order to prepare 1,000 ml. of *N*/10 solution 4 gms. of NaOH are required.

Procedure

Weigh out rapidly by means of a rough balance about 4·2 gms. of solid on a watch glass. Rinse the solid with a little distilled water and dissolve it in distilled water in a beaker, transfer the entire solution into a litre flask. Make the volume up to the mark with distilled water. Shake the flask to have a uniform solution. Close the flask by means of a rubber stopper. This solution is approximately *N*/10. To find the exact strength titrate it against a standard acid using a suitable indicator (*see* p. 219).

CHAPTER III

VOLUMETRIC ANALYSIS

A. Acidimetry and Alkalimetry

By acidimetry we mean the determination of unknown strength of an alkali by titration with a standard acid solution. Alkalimetry is just the reverse of this process. When an acid is mixed with an alkali, H^+ ions of the acid react with OH^- ions of the alkali to produce water. The condition of the solution can therefore be either acidic (when an excess of H^+ ions are present) or alkaline (when an excess of OH^- ions are present) or neutral, *i.e.*, the solution will have a *p*H of 7 (when neither the H^+ ions nor the OH^- ions are present in excess of the equivalent proportions). This is actually what happens in the case of a strong acid and a strong base. The case is otherwise when the acid or the base or both are weak. The solution in that case even at the equivalence point will be either slightly acidic or alkaline instead of being neutral.. This is due to hydrolysis of the salt formed in the neutralisation reaction. The exact value of hydrogen ion concentration of the solution depends upon the nature of the acid and base and on the concentration of the solution. There are some organic substances, which can indicate the termination of a neutralisation process by change of colour. These substances are called neutralisation indicators. A good indicator should give a sharp change of colour when the condition of the solution changes from acidic to alkaline and *vice versa*. Choice of indicators in neutralisation reactions depends on the nature of the acids and bases and also on their concentration. For a titration to be feasible there should be a satisfactory change of *p*H at or near the equivalence point produced by the addition of a small volume of acid or alkali as the case may be and indicator that changes colour at or near the equivalence point should be chosen.

Titration of	Indicators to be used	Colour change Acid-base
(*a*) Hydrochloric acid—caustic soda (*i.e.* strong acid—strong base).	Any indicator, having a colour change between *p*H 3 & 10.	— —

Titration of	Indicators to be used	Colour change Acid-base
(*b*) Acetic acid—caustic soda (*i.e.*, weak acid —strong base).	Phenolphthalein	Colourless—red.
(*c*) Ammonia-sulphuric acid (*i.e.*, weak base —strong acid).	Methyl orange	Red—orange-yellow.
(*d*) Acetic acid—ammonia (*i.e.*, weak acid —weak base).	This titration should be avoided as far as possible, but neutral red-methylene blue indicator may however be used.	— — —

Experiment:

Determination of the strength of H_2SO_4 solution (standardisation of H_2SO_4 solution) by the Na_2CO_3 solution of accurately known strength.

Procedure

Take a clean burette, wash it first thoroughly with distilled water and then rinse it thrice with the given acid taking about 5 ml. portions of the acid for each washing. Fill the burette now with the acid taking care that no air bubble is enclosed in the jet and the lower meniscus of the top level of the liquid just touches the zero mark.

Wash a 250 ml. conical flask thoroughly with distilled water. Take a 25 ml. clean pipette. Wash it first with distilled water and then rinse it thrice with the standard alkali taking about 4-5ml. of the solution for each washing. Transfer 25 ml. of the standard alkali into the conical flask with the help of this pipette. (For technique of this operation *see* General Instructions' p. 213). Add a drop or two of methyl orange into the conical flask containing Na_2CO_3 solution.

Now place the conicial flask upon a piece of unglazed white paper just below the jet of the burette; run in the acid slowly from the burette and rotate the flask constantly. When the colour of the solution contained in the flask becomes faintly yellow, wash the flask down with a little distilled water and continue adding acid very carefully, drop by drop till the solution just turns pink. Note the burette reading.

This first reading may be an approximate one indicating the position of the true end point within 0·2—0·5 ml. Repeat this experiment *three* times. This should yield concordant results and under no circumstances should differ by more than 0·1 ml. Enter you results in the following tabular form and take the mean of the readings:

No. of expt.	Vol. of alkali (taken) in ml.	Vol. of acid required in ml.	Mean
1	25	......	......
2	25	......	......
3	25	......	......
4	25	......	......

Calculation

$$\text{Strength of alkali} \times \text{volume of alkali} = \text{Strength of acid} \times \text{volume of acid}$$

$$\therefore \text{ Strength of acid} = \frac{\textit{Strength of alkali} \times \textit{volume of alkali}}{\textit{Volume of acid}} = x(N) \text{ say.}$$

[$\therefore$ amount of sulphuric acid in gms./litre$=x \times 49$].

Experiment:

Determination of the strength of caustic soda solution by oxalic acid solution of accurately known strength.

Procedure

Take 25 ml. of caustic soda solution in a conical flask. Add a drop or two of phenolphthalein indicator, when the solution turns pink. Titrate it against oxalic acid taken in the burette till the pink colour just disappears. [Run in the major portion of the acid hurriedly and then continue the addition dropwise very cautiously towards the end until with one drop of the acid the pink colour just disappears.] Read the burette and repeat the experiment *three* times. Tabulate the results as before and take the mean of these readings for your calculation.

Calculation

$$\text{Strength of acid} \times \text{volume of acid} = \text{Strength of alkali} \times \text{volume of alkali.}$$

$$\therefore \text{ Strength of alkali} = \frac{\textit{Strength of acid} \times \textit{volume of acid}}{\textit{Volume of alkali}} = x(N) \text{ say.}$$

[Hence amount of NaOH in gms./litre$=x\times 40$]

Note that in order to determine the strength of one acid by another or one alkali by another we require a suitable comparison solution. In the first case two acids are compared with by titration against one common alkali, which serves here the purpose of comparison solution; while in the second case two alkalis are similarly compared with by titration against a common acid (*i.e.*, comparison soln.). The experiment described below will help a student in proper understanding of this process.

Experiment:

Determination of the strength of one acid by another by titrating against a common alkali.

Hydrochloric acid vs. *oxalic acid, comparison solution*: *NaOH*

Procedure

Prepare an approximately decinormal NaOH solution (if not supplied) by weighing out about 4·2 gms. of solid caustic soda by means of a rough balance (*see* preparation of N/10 NaOH solution, p. 216). Take 25 ml. of this solution in a 250 ml. conical flask and titrate with oxalic acid solution (of known strength) taken in the burette using phenolphthalein as indicator. Reapeat the expt. *three* times. Tabulate your results as usual and take the mean of these readings. Wash the burette well with distilled water and then finally with given HCl solution thrice, taking about 4-5 ml. of the solution for each washing.

Wash the conical flask with distilled water only and take 25 ml. of NaOH solution in it. Titrate with given HCl solution taken in the burette using methyl orange or phenolphthalein as indicator. Repeat the titration *three* times; tabulate your results as usual and take the mean of the readings.

Calculation

Let for neutralisation of 25 ml. of alkali the volume (mean value) of oxalic acid required$=x$ ml. and the volume (mean value) of HCl (of unknown strength) required for neutralisation of the same amount of alkali$=y$ ml.

Suppose the known strength of oxalic acid solution$=S_1(N)$ and the strength of HCl solution$=S_2(N)$, which is to be determined.

$$\therefore \quad x \times S_1 = y \times S_2$$

$$\text{or,} \quad S_2 = \frac{x \times S_1}{y} \; (N)$$

$$\left[\quad \therefore \; \text{amount of HCl in gms/litre} = \frac{x \times S_1 \times 36{\cdot}5}{y}. \quad \right]$$

Experiment:

Analysis of commercial caustic soda or analysis of mixed alkali ($NaOH+Na_2CO_3$).

Procedure

(*i*) Take 25 ml. of the given alkali solution in a 250 ml. conical flask and titrate with a standard acid (*e.g.*, standard HCl) in the burette using phenolphthalein as indicator till the pink colour just disappears. Note the volume of acid required. At this stage the whole of caustic soda and half of Na_2CO_3 has been neutralised. Now add a drop or two of methyl orange to the contents in the conical flask, when the solution turns faint yellow. Continue addition of acid dropwise till the yellow colour changes to just pink. Note the volume of acid required in the second stage of titration. This acid has neutralised the remaining half of Na_2CO_3. Repeat the whole expt. *three* times and tabulate the results as usual. Take the mean volume of acid for each of the two sets of titre values.

Calculation

Let V_1 ml. be the volume (mean) of acid required in the titration with phenolphthalein as indicator and V_2 ml. be the volume (mean) of the same acid required in the titration with methyl orange as indicator. Suppose also that the strength of acid$=S(N)$.

Total Na_2CO_3 corresponds to $2V_2$

Hence Na_2CO_3 present in 25 ml. mixed alkali

$\equiv 2V_2$ ml. of $S(N)$ acid$=(2V_2 \times S \times 0{\cdot}053)$ gms.

Whole of NaOH corresponds to $(V_1 - V_2)$.

$\therefore$ NaOH present in 25 ml. mixed alkali$\equiv(V_1 - V_2)$ ml. of $S(N)$ acid $= \{(V_1 - V_2) \times S \times 0{\cdot}04\}$ gms.

(*ii*) The same result can be achieved by a slight modification of the above procedure:

Take 25 ml. portion of the mixed alkali in a 250 ml. conical flask and titrate with standard acid using methyl orange as indicator. The volume of acid at this stage corresponds to total alkali present in the mixture. Let this volume be V ml. If the experiment be carefully done

$$\text{then } V = V_1 + V_2$$

i.e., the acid required in the experiment must be equal to the sum-total of the acid required in the previous experiment.

Titrate another 25 ml. portion of the mixed alkali with standard acid using phenolphthalein as indicator. Let this volume be V_3 ml. The acid required (at this stage) corresponds to whole of NaOH and half of Na_2CO_3.

[Repeat the experiments, tabulate the results as usual and take the mean value of each set of titre values.]

Calculation

Total Na_2CO_3 present in 25 ml. of the mixed alkali

$\equiv 2(V - V_3)$ ml. of $S(N)$ acid

$= \{2(V - V_3) \times S\}$ ml. of (N) acid

$\equiv \{2(V - V_3) \times S\}$ ml. of (N) Na_2CO_3 solution

$= \{2(V - V_3) \times S \times 0{\cdot}053\}$ gms.

Total caustic soda corresponds to $V - 2(V - V_3)$ i.e., $(2V_3 - V)$.

Hence total NaOH present in 25 ml. of the mixed alkali

$\equiv (2V_3 - V)$ ml. of S (N) acid

$= \{(2V_3 - V) \times S\}$ ml. of (N) acid

$\equiv \{(2V_3 - V) \times S\}$ ml. of (N) NaOH solution

$= (2V_3 - V) \times S \times 0{\cdot}04$ gms.

N.B. 1. Note that the acid reacts with NaOH and Na_2CO_3 according to the equations (*a*) and (*b*) respectively:

$$(a)\ NaOH + HCl \rightleftharpoons NaCl + H_2O$$

(*b*) $Na_2CO_3 + HCl = NaHCO_3 + NaCl$

$NaHCO_3 + HCl = NaCl + H_2O + CO_2$.

Hence in the case of caustic soda (and sodium bicarbonate) the formula weight is the equivalent weight and in the case of Na_2CO_3 the equivalent weight is half of the formula weight.

$\therefore$ 1 ml. of (*N*) HCl $\equiv$ 0·04g. NaOH

1 ml. of (*N*) HCl $\equiv$ 0·053g. Na_2CO_3.

$\equiv$ 0·084g. $NaHCO_3$.

2. The equation (*b*) shows that Na_2CO_3 reacts with acids in two stages. Na_2CO_3 is first converted into bicarbonate and at this bicarbonate stage (half-neutralised stage) the *pH* of the solution is about 8·3, when phenolphthalein becomes almost colourless. Thus with phenolphthalein, the point at which half of Na_2CO_3 is neutralised is detected.

3. In order to obtain the amounts of NaOH and Na_2CO_3 in gms./litre multiply the above results by 40, because 25 ml. of the solution was taken for titration.

Experiment:

Determination of a mixture of Na_2CO_3 and $NaHCO_3$

Procedure

Take 25 ml. of the given solution in a 250 ml. conical flask and titrate with standard hydrochloric acid solution using methyl orange as indicator. Repeat the experiment *three* times; tabulate your results as usual and take the mean value for calculation. Let this volume be *V* ml. This corresponds to total alkali ($Na_2CO_3 + NaHCO_3$).

Titrate another 25 ml. portion of the given solution with the same acid using phenolphthalein as indicator. Repeat the experiment as usual. Let the volume (mean value) of the acid required be V_1 ml. This corresponds to half of the sodium carbonate present in the mixture.

Calculation

Suppose the strength of standard acid $= S(N)$

Therefore, total Na_2CO_3 present in the 25 ml. portion of the given solution $\equiv 2V_1$ ml. of $S(N)$ acid.

$=(2V_1 \times S)$ ml. of (N) acid
$\equiv(2V_1 \times S)$ ml. of (N) Na_2CO_3 soln.
$=(2V_1 \times S) \times 0{\cdot}053$g.

And total bicarbonate present in the 25 ml. portion of the given solution$\equiv(V-2V_1)$ ml. $S(N)$ acid
$=\{(V-2V_1) \times S\}$ ml. of (N) acid
$=\{(V-2V_1) \times S\}$ ml. (N) $NaHCO_3$ soln.
$=(V-2V_1) \times S \times 0{\cdot}084$ g.

Multiply each of the above results by 40 in order to obtain the amounts present in one litre, since 25 ml. portion of the solution was taken for titration.

Experiment:

Determination of ammonia in a given solution of ammonium salt.

(*a*) **Procedure**

Take 25 ml. of the given solution of ammonium salt (other than carbonate and bicarbonate) in a 250 ml. (better if the size is bigger) conical flask. Add a measured volume of standard NaOH solution in excess. To avoid mechanical loss place a small funnel in the neck of the flask. Boil the solution and continue heating until no more ammonia evolves. [Hold a piece of filter paper moistened with mercurous nitrate solution in the issuing steam. If ammonia be present, the filter paper turns black.] Cool the flask. Wash the inner side of the flask with a little distilled water. Wash also the funnel and its stem using little distilled water. Take the washing in the flask. Now add a drop or two of methyl red or phenolphthalein and run into the mixture standard solution of hydrochloric acid from a burette.

Calculation

Let the strength of NaOH solution $=S_1(N)$
" " HCl " $=S_2(N)$
Let the volume of NaOH solution added $=V$ ml.
" " HCl solution required $=V_1$ ml.

V_1 ml. of S_2 (N) HCl$=(V_1 \times S_2)$ ml. of (N) HCl solution
$\equiv(V_1 \times S_2)$ ml. of (N) NaOH solution.

Again, V ml. of $S_1(N)$ NaOH solution$=(V \times S_1)$ ml. of (N) NaOH solution.

Hence the volume of NaOH solution that reacted with ammonium salt

$=(VS_1-V_1S_2)$ ml. of (N) NaOH solution.

$\therefore$ amount of ammonia in 25 ml. of the given solution $=(VS_1-V_1S_2)\times 0{\cdot}017$g.

$\therefore$ amount of ammonia in gms/litre of the given solution $=(VS_1-V_1S_2)\times 0{\cdot}017\times 40$.

N.B. With phenolphthalein the solution at first turns pink and the end point of the above titration is indicated when the pink colour just disappears.

With methyl red the solution at first turns yellow and the end point of the titration is indicated, when the solution just turns red.

The reactions that occur in the above expt. are expressed by the following equations:

$$NH_4Cl+NaOH=NH_3+NaCl+H_2O.$$

$$NaOH+HCl=NaCl+H_2O$$

$\therefore$ 1 $NH_4Cl\equiv$1 $NaOH\equiv$1 NH_3

or, 1,000 ml. of (N) NaOH solution$\equiv$17 gms. of NH_3

$\therefore$ 1 ml. of (N) NaOH solution$\equiv$0·017g. NH_3.

(*b*) Method involving the use of formaldehyde

Principle

When an ammonium salt (say NH_4Cl) reacts with formaldehyde, hexamethylene tetramine is formed and an equivalent amount of acid is simultaneously liberated. Hence by titrating the liberated acid with standard alkali, amount of ammonia present in the given ammonium salt solution can be determined.

$$4NH_4Cl+6CH_2O=(CH_2)_6N_4+6H_2O+4HCl.$$

Procedure

Take 25 ml. of the given ammonium salt solution in a 250 ml. conical flask. Add an excess of neutral formaldehyde solution till it smells of formaldehyde. Shake and allow the mixture to stand for five minutes. Titrate with a standard caustic soda solution till the pink colour just appears.

Calculation

Let the volume of NaOH required $= V$ ml.

and the strength of NaOH solution $= S(N)$

V ml. of $S(N)$ NaOH solution $= (V \times S)$ ml. of (N) NaOH soln.

$\therefore$ amount of ammonia in 25 ml. of the given ammonium salt solution $= V \times S \times 0{\cdot}017$ g.

$\therefore$ amount of ammonia in gms./litre of the given solution $= V \times S \times 0{\cdot}017 \times 40$.

N.B. 1. *Preparation of neutral formaldehyde*:

To the formaldehyde solution supplied add a drop or two of phenolphthalein and then add caustic soda solution dropwise till a faint pink colour *just* appears. Use the neutral solution thus prepared.

2. Wash the burette first with dil. acid and then with water immediately after the completion of titration, because caustic soda solution attacks glass.

[*Note that in all the above cases of estimation, it is desirable that the volume of the solution taken in a flask should be made up to a workable one (i.e., about* 50 *ml. or a little more) by dilution, if necessary, with proper quantity of water before allowing it to react with the other reactant taken in the burette. This will prove advantageous for stirring the solution during titration and noting the colour change through the whole mass of solution.*]

CHAPTER IV

VOLUMETRIC ANALYSIS : B. REACTIONS IN WHICH CHANGE OF VALENCY OCCURS

Oxidimetry and Reductimetry

The equivalent weight of an oxidising or reducing agent is defined as the parts by wt. of the substance which combine with or contain 1·008 parts by weight of (available) hydrogen or 8·000 parts by wt. of (available) oxygen or its equivalent. Let us take, for examples, the case of $KMnO_4$ and $K_2Cr_2O_7$, the equivalent weight of which can be calculated with the help of the following equations:

(*i*) $2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5\dot{O}$.

or (the hypothetical equation) $2KMnO_4=K_2O+2MnO+5O$.

(*ii*) $K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O$,

or (the hypothetical equation) $K_2Cr_2O_7=K_2O+Cr_2O_3+3O$.

Thus we see that in the acid medium two molecules of $KMnO_4$ supplies 5 atoms of oxygen and hence the equivalent weight of $KMnO_4=\frac{2KMnO_4}{10}=\frac{2\times158}{10}=31{\cdot}6$. And the equivalent weight of $K_2Cr_2O_7=\frac{K_2Cr_2O_7}{6}=49{\cdot}04$, since in the acid medium one molecule of $K_2Cr_2O_7$ supplies 3 atoms of oxygen [*see* the equation (*ii*) above].

The above treatment though useful for beginners is limited in application. A more general approach is to consider the oxidation; a process, which results in the loss of one or more electrons by atoms or ions, while reduction is one that involves the gain of one or more electrons by atoms or ions. In the light of this electronic theory, a more general definition of the equivalent weight is :

The equivalent weight of an oxidant or a reductant is the molecular weight of the compound divided by the total number of electrons that are gained or lost in a raction by the oxidising or reducing ion respectively per one molecule of the substance. The partial ionic equations for the normal reduction of $KMnO_4$ and $K_2Cr_2O_7$ in acid medium can be expressed as follows:

$$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$$
$$Cr_2O_7^{--} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$$

$$\therefore \text{ Eq. weight of } KMnO_4 = \frac{KMnO_4}{5}.$$

$$\text{and} \quad \text{,,} \quad K_2Cr_2O_7 = \frac{K_2Cr_2O_7}{6}.$$

Similarly, for the oxidation of ferrous ion to ferric ion, the following partial ionic equation can be written:

$$Fe^{++} - e = Fe^{+++}$$

$$\therefore \text{ Eq. wt. of ferrous salts} = \frac{\text{Mol. wt. of ferrous salt}}{1}.$$

Hence in the redox process the equivalent weight and molecular weight of a ferrous salt are identical.

Since the equivalent weight depends upon the reaction concerned, it should be noted here that the same substance may have different equivalent weights. Reduction of $KMnO_4$ in neutral medium, for example, can be expressed by the following partial ionic equation:

$$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^-.$$

Hence eq. wt. of $KMnO_4$ here is 1/3 mol. wt. and not 1/5 mol. wt. as in the acid medium. Again oxidation of potassium tetroxalate $KHC_2O_4, H_2C_2O_4 \cdot 2H_2O$ is represented by the following partial ionic equation: $C_2O_4^{--} - 2e \longrightarrow 2CO_2$. Since in a gm. molecule there are two $C_2O_4^{--}$, the eq. wt. of tetroxalate is here 1/4 mol. wt. But the neutralisation of potassium tetroxalate by caustic soda is expressed as:

$$KHC_2O_4, H_2C_2O_4.2H_2O + 3NaOH = KNaC_2O_4, Na_2C_2O_4 + 5H_2O.$$

Hence the eq. wt. of the same tetroxalate in this reaction is 1/3 mol. wt. and not 1/4 mol. wt. as in oxidation of tetroxalate. Thus, we can see that the same substance may have different equivalent weights.

(*a*) **Methods involving the use of oxidation with potassium permanganate:**

Preparation of standard (N/10) oxalic acid solution: *see* p. 215.

Preparation of standard (N/10) sodium oxalate solution: The partial ionic equation for oxidation of both oxalic acid and sodium oxalate is expressed as follows:

$$C_2O_4^{--} - 2e = 2CO_2.$$

Hence the equivalent weight of both sodium oxalate and oxalic acids is half of their respective molecular weights. Molecular weight of sodium oxalate is 134 and equivalent weight is therefore, $\frac{134}{2} = 67$. Hence in order to prepare 250 ml of 0·1(*N*) solution of sodium oxalate 1·675 gms. of the pure substance are required. $\left[\frac{67}{4 \times 10} = 1{\cdot}675 \text{ g}\right]$

Procedure

Weigh out accurately about 1·7g. of pure sodium oxalate into a clean 250 ml. measuring flask fitted up with a funnel. Wash down the whole of sodium oxalate by careful addition of distilled water. Now hold the flask firmly and shake well. Add some dil. H_2SO_4 to make the dissolution complete. When all the solid has dissolved make the volume up to the mark.

Let the wt. of sodium oxalate taken $= W$ gms.

∴ Strength of oxalate solution thus prepared

$$= \frac{W}{1{\cdot}675} \; N/10$$

[Calculate up to 4th. place of decimal.]

N.B. It may be rather difficult to dissolve sodium oxalate in water alone. Addition of some dil. H_2SO_4 will be effective. Sodium oxalate may however be dissolved directly in 0·5 (*N*) H_2SO_4.

Preparation of standard (N/10) Mohr's salt $FeSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$ (Ferrous ammonium sulphate) solution:

The partial ionic equation for oxidation of ferrous ion to erric state is expressed as follows:

$$Fe^{++} - e = Fe^{+++}.$$

With ferrous ammonium sulphate one ferrous ion per molecule of the salt is oxidised to ferric state by loss of only one electron. Hence the eq. wt. of this substance is the same as the molecular weight, which is 392. In order to prepare, therefore, 250 ml. of 0·1 (*N*) solution of Mohr's salt 9·8 gms. of pure salt are required. $\left[\frac{392}{4\times 10} = 9{\cdot}8\text{g.}\right]$

Procedure

Weigh out accurately about 9·8 gms. of pure salt in a 250 ml. flask. Dissolve the salt directly in H_2SO_4(0·5 *N* to 1*N*) by careful shaking. When all the solid has dissolved, make up the volume to the mark by careful addition of same acid.

Let the wt. of the substance taken $= W$ gms.

$\therefore$ Strength of the solution thus prepared $= \frac{W}{9{\cdot}8}\left(\frac{N}{10}\right)$

[Calculate up to 4th. place of decimal]

N.B. 1. Note that ferrous sulphate is easily oxidised by air (on exposure) to basic ferric sulphate. To stabilise ferrous sulphate it is crystallised with ammonium sulphate and the product ferrous ammonium sulphate is used instead of ferrous sulphate.

2. In precision work ferrous ammonium sulphate cannot be used as a primary standard due to uncertainty of its purity.

Preparation of 0·1 N Potassium permanganate solution:

It has already been shown that the equivalent weight of $KMnO_4$ is 31·6. Hence to prepare 1 litre of approximately 0·1 (*N*) solution about 3·2 gms. of the substance are required.

Procedure

Weigh out on a watch glass about 3·2 gms. of finely powdered $KMnO_4$ of analytical reagent quality. Transfer the entire solid into a big beaker (500 ml.). Add warm distilled water and shake. Now decant the clear solution from the top into a litre flask. Repeat this operation of dissolving out the solid by shaking with warm distilled water added in portions (taking care that the total volume of the solution is *always* less than 1 litre) till nearly all the solid has dissolved. Then shake the flask vigorously and finally make up the volume to the mark with more distilled water. Shake well, stopper the flask and keep away from direct light (better dark) except when in use. The solution thus prepared is approximately 0.1 (N). Determine the exact strength by titrating against standard oxalic acid or *better* sodium oxalate solution (of accurately known strength) before use.

N.B. Potassium permanganate is not used as a primary standard because of the following reasons:

(*i*) It is not usually obtained in a very pure state and free from manganese dioxide.

(*ii*) The presence of manganese dioxide catalyses the auto-decomposition of $KMnO_4$ solution.

(*iii*) Moreover, $KMnO_4$ being a strong oxidising agent a portion of the reagent is used up in oxidising the oxidisable impurities present in reagents or distilled water. It can also undergo photochemical decomposition.

(*iv*) Filtration is preferable to decantation. This may be done by: (*a*) passing through a Gooch containing a pad of purified asbestos, (*b*) passing through a plug of purified glass wool in a funnel; etc.

Experiment:

Determination of strength of $KMnO_4$ solution (standardisation)

(*a*) *Standardisation against oxalic acid (or sodium oxalate) solution:*

Procedure

Take 25 ml. of standard oxalic acid (or sodium oxalate) solution in a 500 ml. concial flask (or beaker). Add 150 ml. of 2(N) H_2SO_4.

Heat to about 80°C. Run in the permanganate solution from an all glass burette into this hot solution, with constant stirring and see that the temperature of the solution may not fall below 60°C during titration. At first, add permanganate in small quantities at a time. But towards the end, take care to allow each drop to be completely decolourised before the next is introduced. Stop addition of $KMnO_4$, when just one drop imparts pink colour to the whole mass of the solution.

Note that the pink colour after lasting for 30 secs. may disappear again. Note the volume of $KMnO_4$ solution added. Repeat* the titration *twice*, at least.

Calculation

Let the strength of oxalic acid solution $= S(N)$
and volume of $KMnO_4$ solution added $= V$ ml.

$$\therefore \text{ Strength of } KMnO_4 = \frac{S \times 25}{V} (N)$$

*In subsequent titrations addition of 90-95% of the titrant prior to heating is advocated by some authority.

N.B. (*i*) Prepare approximately $(2N)$ H_2SO_4 by cautious addition of about 25 ml. of conc. acid to 425 ml. of water and use 150 ml. of this acid for each titration.

(*ii*) Always note the upper meniscus of $KMnO_4$ (and in fact for all densely coloured) solution.

(*iii*) Oxidation of oxalic acid by permanganate is represented by the following equation:

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

Decolourisation of $KMnO_4$ is slow in the beginning but becomes rapid with the formation of $MnSO_4$, which, therefore, acts as a catalyst. Hence, at the beginning the titration should be slow enough to have sufficient Mn^{+2}ions.

(*b*) *Standardisation against ferrous ammonium sulphate*:

Procedure

Take 25 ml. of ferrous ammonium sulphate solution in a 500 ml. conical flask. Add about 35-40 ml. of 6 (N) H_2SO_4. Dilute to 150 ml. with water. Run in the permanganate solution from the burette till a faint pink colour develops throughout the whole mass of the solution.

Calculation

Let the strength of ferrous salt solution $= S(N)$
Volume of $KMnO_4$ solution $= V$ ml.
Strength ,, ,, $= S_1 (N)$

$$\therefore 25 \times S = V \times S_1$$

or, strength of $KMnO_4$ solution, i.e., $S_1 = \frac{S \times 25}{V} (N)$

N.B. (*i*) Stir the contents of the conical flask (by giving swirling motion) constantly during titration.

(*ii*) Note the first appearance of the permanent faint pink colour.

(*iii*) It is advisable to add about 2 ml. of syrupy phosphoric acid, as it makes the colour change more sharp at the end-point by forming colourless complex $[Fe(HPO_4)]^+$

Experiment:

Determination of the amount of iron per litre in a given ferrous-iron solution using a standard permanganate solution.

Procedure:

Take 25 ml. of the given solution in a 500 ml. conical flask. Add 35-40 ml. of 6(*N*) H_2SO_4. Dilute to 150 ml.; titrate with $KMnO_4$ solution till the first permanent pink colour develops throughout the whole mass of the solution. Repeat the experiment *two* times. Take the mean of these values for your calculation. Determine also the exact strength of the given permanganate solution in the usual way.

Calculation

Let the exact strength of given permanganate solution as determined by experiment $= S(N)$ and
the volume of $KMnO_4$ solution required to oxidise 25 ml. of ferrous iron solution $= V$ ml.

Since 1 ml. of (N) $KMnO_4$ solution $\equiv 0{\cdot}056$g. of Fe
1 ml. of $S(N)$ $KMnO_4$ solution $\equiv (0{\cdot}056 \times S)$g. of Fe
$\therefore$ V ml. $S(N)$ $KMnO_4$ solution $\equiv (0{\cdot}056 \times S \times V)$g. of Fe
or, 25 ml. of ferrous iron solution $\equiv (0{\cdot}056 \times S \times V)$ g. of Fe.
$\therefore$ Iron present per litre $= (0{\cdot}056 \times S \times V \times 40)$ gms.

The result can also be expressed in terms of gms. of Mohr's salt per litre as follows :

56g. of Iron $\equiv$ 392g. of Mohr's salt
or, 0·056g. ,, $\equiv$ 0·392g. ,, ,,
$\therefore$ Mohr's salt present per litre
$= 0{\cdot}392 \times S \times V \times 40$g.

Similarly, the result can be expressed in terms of gms. of $FeSO_4 . 7H_2O$ per litre, as 56g. of Iron=278g. of $FeSO_4 . 7H_2O$.

N.B. (*i*) Here also the colour change at the end point is much improved by addition of a few ml. of syrupy phosphoric acid.

(*ii*) In presence of chloride ions, the ferrous iron solution cannot be titrated as such with $KMnO_4$ solution. In such a case don't add phosphoric acid but add about 20 ml. of Reinhardt solution before titrating with $KMnO_4$ solution.

Experiment:

Determination of the amount of iron per litre of a given ferric iron (or, a mixture of ferric and ferrous iron) solution with permanganate solution.

Principle

Ferric iron is first completely converted into ferrous state by means of a suitable reducing agent and after the removal of excess of reducing agent the ferrous salt is converted (oxidised) to ferric state again by titrating with a standard solution of $KMnO_4$. The hot solution of ferric chloride, for example, when treated with stannous chloride solution in a medium which is 5—6 (N) with respect to hydrochloric acid, is quantitatively reduced to ferrous chloride.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The ferrous ion is then oxidised to ferric state by allowing it to react with $KMnO_4$ solution under suitable condition.

Procedure

Take 25 ml. of the solution in a 500 ml. conical flask. Add 20 ml. conc. HCl and heat just to boiling. Remove the source of heat, add dropwise concentrated solution of $SnCl_2$ till the yellow colour of the solution has nearly disappeared and then add a more dil. solution of $SnCl_2$ (prepared by mixing one volume of $SnCl_2$+2 volumes of dil. HCl) drop by drop till the yellow colour disappears (avoid large excess of $SnCl_2$). Shake after each addition of $SnCl_2$. *Cool* rapidly to room temperature under the tap. Add about 10 ml. of a saturated solution of $HgCl_2$—all at a time with shaking and allow to stand for 5 minutes. A slight silky white ppt[1]., should appear at this stage. Dilute to about 300 ml. with distilled water. Add 25 ml. of Zimmermann[2]—Reinhardt solution. Titrate the mixtrue slowly and with constant stirring with $KMnO_4$ solution till the first pink colour develops throughout the bulk of the mixture. The pink colour fades away after 15 seconds. Note the volume of $KMnO_4$ solution, which corresponds to whole of iron (Ferric+Ferrous). Repeat the experiment *at least two times.*

Calculation: *See* the calculation of the previous experiment.

Notes 1. The little excess of $SnCl_2$ added reduces mercuric chloride to mercurous chloride, which is precipitated in the shape of silky white suspension.

$$2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4.$$

Hence a white ppt. indicates that an excess of stannous chloride has been added. Should no ppt. appear on addition of $HgCl_2$, it is most likely that the amount of $SnCl_2$ added is **not sufficient** enough to reduce the whole of ferric iron to ferrous iron. If, on the other hand, a heavy white ppt. or a grey (or black) ppt. appear, *too much* of $SnCl_2$ has been added. In either case, the result will be inaccurate. Throw away the solution and start the experiment anew.

2. The redox potential of:

MnO_4'/Mn^{++}	is 1.52 volts
Fe^{+++}/Fe^{++}	is 0.77 volt
$Cl_2/2Cl^-$	is 1.36 volts

Thus, permanganate being a strong oxidising agent oxidises not only Fe^{++} ions (Fe^{++} to Fe^{+++}) but also tends to oxidise Cl' ion (Cl' to Cl_2). Besides, this latter reaction (*i.e.*, change of $Cl' \rightarrow Cl_2$), which is an undesirable side reaction is induced by the former reaction (*i.e.*, Fe^{++} to Fe^{+++} by MnO_4').

The manganous sulphate (*i.e.*, Mn^{++} ions) present in Reinhardt solution reduces the redox potential of MnO_4'/Mn^{++} system making $KMnO_4$ a weaker oxidising agent and the Cl' ions in consequence are prevented from being oxidised by MnO_4' ions. But the above explanation now appears to be inadequate. Mn (III) seems to be always involved in the reduction of Mn(VII) i.e., permanganate ion to Mn(II). The protective solution Z-R, as it is called, provides sufficient concentration of Mn(II) to react with any local excess of permanganate and thus the reduction of any intermediary states of manganese to Mn(III) is also ensured. The potential determining system is actually the Mn (III) -Mn(II) couple. The Mn (III) - Mn(II) potential is lowered largely by phosphoric acid and to a smaller extent by sulphuric acid. A depressant effect upon the potential is, of course, exercised by Mn(II) also, so that Fe(II) rather than chloride is oxidised by (Mn(III). This reduction in redox potential however decreases the effectiveness of MnO_4' ion as an oxidising agent towards Fe^{++} ions too.

But phosphoric acid, *i.e.*, PO_4''' ions added remove yellow-coloured Fe^{+++} ions in the form of colourless complex ions and thus also the redox potential of Fe^{+++}/Fe^{++} system is reduced and consequently the reducing power of Fe^{++} ion is increased; while the redox potential of $Cl_2/2Cl'$ remains unaffected. Moreover, Mn^{++} ions act as a positive catalyst in the oxidation of Fe^{++} to Fe^{+++} by $KMnO_4$. Another less important function of PO_4''' ions is to make the end-point more clearly visible, the yellow-coloured Fe^{+++} ions as has already been stated being removed in the form of colourless complex ion.

Experiment

Determination of the amount of calcium per litre in the solution supplied.

Principle

Calcium is precipitated from the known volume of the given solution as oxalate. The precipitated oxalate on being treated with dil sulphuric acid, oxalic acid is liberated. The liberated acid is titrated with standard $KMnO_4$ solution.

$$CaC_2O_4+H_2SO_4=CaSO_4+H_2C_2O_4 \quad \ldots \quad \ldots \quad (i)$$

$$2KMnO_4+3H_2SO_4+5H_2C_2O_4$$
$$=K_2SO_4+2MnSO_4+10CO_2+8H_2O \quad \ldots \quad \ldots \quad (ii)$$

From eqn. (*ii*) 1/5 mol. of $KMnO_4 \equiv \frac{1}{2}$ mol. of oxalic acid.

Again from eqn. (*i*) $\frac{1}{2}$ mol. of oxalic acid $\equiv \frac{1}{2}$ mol. of CaC_2O_4

$\therefore$ 1/5 mol. of $KMnO_4 \equiv \frac{1}{2}$ mol. of oxalic acid $\equiv \frac{1}{2}$ mol. of CaC_2O_4.

$\therefore$ 1,000 ml. (*N*) $KMnO_4$ solution $\equiv \frac{1}{2}$ mol. of oxalic acid, which can be obtained from $\frac{1}{2}$ mol. of CaC_2O_4.

$\therefore$ 1,000 ml. of (*N*) $KMnO_4 \equiv 20$ gms. of calcium

Thus 1 ml. of (*N*) $KMnO_4 \equiv 0.020$ g. of calcium.

Procedure

Take 25 ml. of the given calcium solution in a 500 ml. beaker. Dilute to about 200 ml. of with distilled water and add 2-3 drops of methyl orange indicator. Add 10 ml. of dil. HCl (1:1), when the solution turns pink. Heat the solution to boiling. Add to this hot solution about 25 ml. of hot solution of ammonium oxalate containing 1g. of ammonium oxalate solid with constant stirring. To the hot mixture (70°—80°) add dil. solution of ammonium hydroxide (1 : 1) dropwise with constant stirring till the mixture is faintly alkaline (indicated by yellow colour of the solution). A white ppt. of calcium oxalate comes down. Heat the mixture to boiling and allow to stand for half an hour (preferably one hour) on an asbestos board over a small flame. Add a few more drops of ammonium oxalate solution to the clear solution on the top to see if the precipitation is complete[2]. Decant the supernatant liquid down a glass rod through a quantitative filter paper (Whatman No. 40). Don't pour too much of the solution on to the filter paper at a time and see that the upper level of the solution is always about 1 cm. below the rim of the paper in the filter. Wash down the inner side of the beaker with little hot water taking care that the volume of the wash-liquid is just sufficient to cover up the ppt. Gently swirl, allow to stand for a few minutes and then decant the liquid into the filter. Repeat the process 3-4 times, pour each washing after the previous one is completely drained off and then transfer the ppt. on to the filter. Now wash the ppt. on the filter paper several times using small quantities of cold distilled water every time till the washing[3] is free from chloride and oxalate [test the filtrate with (*i*) $CaCl_2$ solution to which a little NH_4OH was added (better add one or two drops of washing to dil. solution of $KMnO_4$ acidified with dil. H_2SO_4, the presence of oxalate will be indicated by the disappearance of pink colour of $KMnO_4$ on warming) and (*ii*) $AgNO_3$ solution respectively].

Place the beaker in which calcium oxalate was precipitated below the funnel containing the ppt. in such a manner so that the stem of the funnel just touches the innerside of the beaker. Pierce a hole in the apex of the filter paper with a pointed glass rod (taking care that not a bit of the filter paper falls into the beaker) and wash down the ppt. with a jet of hot water into the beaker. Treat the filter with hot 4(N) H_2SO_4 by pouring the acid in small quantities at a time on to the filter. Finally, wash the filter several times thoroughly with hot water so that all the oxalate has been washed down. Add a few ml. more of the diluted acid, if necessary, for getting a clear solution.

Dilute the solution to about 200 ml. Heat it to about 80°C and titrate in the usual way by cautious[1] addition of $KMnO_4$ solution from the burette.

Calculation

Let 25 ml. of the calcium solution

$$\equiv V \text{ ml. of } S(N)\ KMnO_4 \text{ solution.}$$

$\therefore$ 25 ml. of the calcium solution contains

$$V \times S \times 0{\cdot}02\text{g. of calcium.}$$

Hence the amount of calcium per litre

$$= V \times S \times 0{\cdot}02 \times 40\text{g.}$$

N.B. 1. Note that within the time limit the repetition of the experiment not being feasible, the titration with $KMnO_4$ solution should be carried out very cautiously .

2. Ammonium oxalate must be present in large excess.

3. Avoid excessive washing, since calcium oxalate is slightly soluble in water.

(β) Methods involving the use of oxidation with Potassium dichromate.

Unlike potassium permanganate, $K_2Cr_2O_7$ is obtainable in the purest form and stable up to its fusion point. Moreover, the aqueous solution keeps well for an indefinite period. Hence $K_2Cr_2O_7$ solution can be used as a primary standard. A standard solution of $K_2Cr_2O_7$ of accurately known strength is prepared by dissolving a weighed amount of the pure and dry salt in a proper volume of water.

Preparation of standard solution of $K_2Cr_2O_7$.

The oxidation reaction with $K_2Cr_2O_7$ in acid solution is represented by the following equation :

$$Cr_2O_7'' + 14H^+ + 6e = 2Cr^{+++} + 7H_2O.$$

Hence the equivalent weight of $K_2Cr_2O_7$ is 1/6th. of the molecular weight, *i.e.*, $\frac{294{\cdot}21}{6} = 49{\cdot}035$. Therefore, in order to prepare 250 ml. of $K_2Cr_2O_7$ solution of $\frac{N}{10}$ order, about $\frac{49{\cdot}035}{4 \times 10}$ g., *i.e.*, 1·2258g. of the salt are to be taken.

Procedure

Weigh out about 1·225g. of the pure and dry powdered salt in a 250 ml. volumetric flask. Dissolve in and finally make up the volume with distilled water in the usual way.

Calculation

Let the weight of $K_2Cr_2O_7$ taken $= W$ gms.

$\therefore$ Strength of the solution prepared $= \frac{W}{1{\cdot}2258}\left(\frac{N}{10}\right)$

Experiment

Determination of the amount of ferrous iron per litre in a given ferrous iron solution.

Procedure

Take about 200 ml. of water in a 500 ml. conical flask. Add cautiously about 10 ml. conc. H_2SO_4 acid with 5 ml. syrupy phosphoric acid; cool and add from a pipette 25 ml. of the given ferrous solution. Now add 5-6 drops of diphenylamine indicator. Run in from the burette standard dichromate solution giving a constant swirling motion to the flask till the solution in the flask becomes green. Then add dichromate dropwise. Rotate the flask after each addition and note the effect of previous drop before adding in the next. The end-point is indicated when only with one drop of dichromate the whole solution in the flask assumes a permanent blue violet coloration. Take the burette reading and repeat the experiment at least twice. [The readings should not differ by more than 0·1 ml.]. Note the mean value and deduct 0·05 ml. (which is used up by the indicator itself) from the mean to get the actual volume of dichromate required for oxidation of ferrous iron.

Calculation

Let 25 ml. of ferrous iron solution

$\equiv V$ ml. of $S(N)$ $K_2Cr_2O_7$ solution.

$\therefore$ 25 ml. of ferrous iron solution contains

$V \times S \times 0{\cdot}056$g. of iron.

Hence the amount of iron per litre in the given solution of ferrous iron $= V \times S \times 0{\cdot}056 \times 40$g.

N.B. Once the end-point is determined with certain amount of accuracy, add the indicator very close to the end-point while repeating the experiment.

Note: The indicator action of diphenylamine is dependent on:

(*i*) its oxidation first to colourless diphenylbenzidine, which (*ii*) is reversibly further oxidised to diphenylbenzidine violet.

Note also that the redox potential or the change-potential as it is called of the system II (*i.e.*, diphenylbenzidine violet-diphenylbenzidine) is 0·76 volt at 25°, while that of Fe^{+3}/Fe^{+2} is of 0·77 volt. Hence in order to get correct result the redox potential of ferric/ferrous system must be reduced well below the normal value of 0·77 volt so that the potential at the equivalence point coincides nearly with that of the indicator. This is achieved by adding phosphoric acid, which removes ferric ions in the form of colourless complex and thus lowers sharply the redox potential of ferric/ferrous system.

Experiment

Determination of the amount of ferric iron per litre in a given ferric iron solution.

Procedure

Take 25 ml. of the given ferric iron solution in a 500 ml. conical flask. Add 25 ml. of conc. HCl. Reduce ferric iron with stannous chloride and remove excess of $SnCl_2$ by treatment with $HgCl_2$ (*see* the method involving the use of $KMnO_4$).

Dilute the solution to 200 ml. add 5 ml. syrupy phosphoric acid and 5-6 drops of diphenylamine indicator. Titrate in usual way with dichromate to permanent violet-blue coloration. Take the burette reading and carry out two further titrations (*see* 'ferrous iron—dichromate' titration) at least. Note the mean of the readings and subtract 0·05 ml. from this mean value to get actual volume of $K_2Cr_2O_7$ required.

Calculation

Same as in the preceding experiment.

N.B. Note that the volume of dichromate corresponds to total iron, *i.e.*, ferrous+ferric, if a mixture of the two be given.

(γ) Iodometry—**Methods involving the use of reduction by iodide.**

In iodometric estimation the amount of iodine liberated in a chemical reaction is determined by titration with a standard solution of a suitable reducing agent. The standard redox potential of the system $I' \rightleftharpoons \frac{1}{2}I_2 + e$ at 25°C is 0·53 volt, which shows that iodine is a weaker oxidising agent than $KMnO_4$, $K_2Cr_2O_7$ etc. Strong reducing agent like sodium thiosulphate can quantitatively reduce iodine. If a strong oxidising agent be treated with an excess of iodide ions in acid solution, the oxidant is quantitatively reduced and an equivalent amount of iodine is liberated. Upon titration of this iodine, therefore, the amount of oxidising agent is found out.

Preparation of standard solution of sodium thiosulphate

Sodium thiosulphate $Na_2S_2O_3 \cdot 5H_2O$ though obtainable in a pure state is not suitable as a primary standard because of its efflorescent nature and instability of the solution.

It reacts with iodine according to the following equation:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

Evidently the equivalent weight of sodium thiosulphate is its molecular weight. The same result is obtained in another way. Thiosulphate acts as a reducing agent (*i.e.*, it undergoes oxidation) by virture of the following reaction :

$$2S_2O_3'' - 2e \rightarrow S_4O_6''$$

Two molecules lose 2-electrons and the equivalent wt. of thiosulphate, therefore, is its molecular weight, which is 248·2.

Procedure

To prepare 250 ml. of approximately 0·1*N* solution weigh out about 6·2 gms. of the solid in a rough balance and transfer it into a 250 ml. volumetric flask. Dissolve it in distilled water by shaking and make up the volume as usual. Put in a stopper, shake well and keep aside (preferably in the dark).

Standardisation of sodium thiosulphate solution

(*i*) *Potassium permanganate method**:

Principle

When $KMnO_4$ is treated in acid solution with an excess of potassium iodide, the former is quantitatively reduced and an equivalent amount of iodine is liberated.

$$2KMnO_4+10KI+16HCl=2MnCl_2+5I_2+12KCl+8H_2O.$$

The liberated iodine is titrated with thiosulphate solution. From the known strength of $KMnO_4$ solution, the strength of thiosulphate solution is calculated.

Procedure

In a 250 ml. conical flask, take 50 ml. water, 5-6 gms. of iodate-free potassium iodide and give a swirling motion to the liquid to dissolve the solid. Run in 25 ml. of a standard solution of potassium permanganate from a pipette, add 2-3 ml. of conc. HCl. The liquid turns red due to liberation of iodine. Cover the flask with a watch glass and keep it in the dark for about 5-10 minutes. Wash down with distilled water the bottom of the watch glass and the inside of the flask. Run in sodium thiosulphate solution from a burette into the mixture, whilst swirling the flask constantly till the solution assumes a faint straw-yellow colour. Add 2 ml. of starch solution, when the colour becomes blue. Continue addition of thiosulphate solution dropwise, swirling the liquid constantly till the blue colour is just destroyed. Take the burette reading and carry out two further titrations with two other 25 ml. of portions of $KMnO_4$ solution. Take the mean of the readings.

Calculation

Let 25 ml. of $S_1(N)KMnO_4$ solution

$$\equiv V_2 \text{ ml. } S_2(N) \text{ sodium thiosulphate solution.}$$

$$\therefore V_2 \times S_2 = 25 \times S_1$$

$$\therefore S_2 = \frac{25 \times S_1}{V_2}(N)$$

Note that 1 ml. of (N) Na_2S_2O $\equiv$ 0·03161g. $KMnO_4$.

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*Note that the method is the *least* reliable and hence should be avoided as far as possible.

(*ii*) *Potassium dichromate method :*

Principle

When $K_2Cr_2O_7$ is treated in acid solution with an excess of potassium iodide, the former is quantitatively reduced and an equivalent amount of iodine is liberated.

$$K_2Cr_2O_7+6KI+14HCl=2CrCl_3+3I_2+8KCl+7H_2O.$$

The liberated iodine is titrated with thiosulphate solution. From the known strength of $K_2Cr_2O_7$ solution, the strength of thiosulphate is calculated.

Procedure

Take 25 ml. of $K_2Cr_2O_7$ solution in a 500 ml. conical flask. Add 10 ml. (6*N*) HCl, and 3 gms. of iodate-free KI dissolved in 10 ml. water and give a swirling motion to the liquid. The liquid mixture turns dark-red due to liberation of iodine. Cover the flask with a watch-glass and keep it in the dark for 5 minutes. Wash down with distilled water the bottom of the watch glass and inside of the conical flask. Dilute with distilled water to about 250 ml. Run in sodium thiouslphate solution from a burette whilst giving a swirling motion to the flask. till the liquid becomes yellowish green. Add 2 ml. of starch solution, when the colour becomes blue. Wash down the inside of the flask with little distilled water and continue addition of thiosulphate solution dropwise with constant rotation of the flask till with one drop the colour of the solution changes from blue to light green. Note the burette reading and carry out at least two further titrations with other 25 ml. portions of the dichromate solution. Take the mean of the readings.

Calculation

Let 25 ml. of $S_1(N)K_2Cr_2O_7$ solution

$\equiv V_2$ ml. of S_2 (*N*) sodium thiosulphate soln.

$$\therefore\ V_2\times S_2=25\times S_1$$

$$\therefore\ S_2=\frac{25\times S_1}{V_2}\,(N)$$

Note that 1 ml. of (*N*) $Na_2S_2O_3\equiv0{\cdot}049$g. $K_2Cr_2O_7$ $\equiv0{\cdot}01733$g. Cr.

N.B. The excess of iodide which is always present in the system reacts with acid and hydriodic acid is formed. Hydriodic acid undergoes oxidation by air especially in presence of chromic salt. Hence, it is necessary for accurate work to add 2 gms. of pure $NaHCO_3$ after the addition of KI to maintain an atmosphere of CO_2 within the flask.

Experiment

Determination of strength of potassium dichromate [or amount in gms. per litre] in a given solution of unknown strength.

Procedure

Prepare a solution of $K_2Cr_2O_7$ ($0{\cdot}1N$ order) by weighing out the solid accurately and then dissolving it in a proper volume of water (*see* p. 239). Standardise a solution of sodium thiosulphate against this dichromate solution of accurately known strength. Estimate the $K_2Cr_2O_7$ solution supplied against this standardised thiosulphate solution iodometrically.

Calculation

Same as in the preceding experiment. Multiply the strength (in normality) by equivalent weight to get the amount present in gms/litre.

Alternative method of calculation—

Let 25 ml. solution of $K_2Cr_2O_7$ of unknown strength

$\equiv V$ ml. of $S(N)$ sodium thiosulphate solution

$=(V\times S)$ml. of (N) thiosulphate solution

$\equiv V\times S\times 0{\cdot}049$g. of $K_2Cr_2O_7$

[since 1 ml. of (N) sodium thiosulphate$\equiv 0{\cdot}049$g. of $K_2Cr_2O_7$]

$\therefore$ amount of $K_2Cr_2O_7$ per litre in the given $K_2Cr_2O_7$ solution$=(V\times S\times 0{\cdot}049\times 40)$g.

Experiment

Determination of copper (in gms/litre) in a given solution by sodium thiosulphate.

Principle

A cupric salt solution on being treated with an excess of potassium iodide, iodine is liberated and cuprous iodide is precipitated under the experimental conditions stated below. By estimating the iodine liberated, therefore, the quantity of copper can be determined. The reaction between cupric salt and iodide is represented by the following equation:

$$2Cu^{++}+4I'=Cu_2I_2+I_2.$$

Equivalent weight of copper in this reaction is its atomic weight, which is 63·57, since 1 atom of iodine is liberated for each atom of copper.

Hence, 1 ml. of (*N*) thiosulphate solution≡0·06357g. of Cu.

Procedure

Take 25 ml. of copper solution in a 500 ml. conical flask. Add dil. solution of ammonium hydroxide slowly till a slight permanent turbidity just forms. Add 5 ml. glacial acetic acid, shake, cool and add 3 gms. of iodate-free potassium iodide. A ppt. appears and the solution becomes dark brown. Run in immediately the standard solution of thosulphate from a burette (while swirling the mixture constantly) till the brown colour due to iodine changes to pale yellow. Dilute to 100 ml. and add 2 ml. of starch solution, (and one or two drops of 0·1*N* $AgNO_3$, if possible) when the mixture becomes blue. Continue addition of thiosulphate dropwise with constant swirling of the mixture till the blue colour begins to fade; then add about 1·5—2 gm. of ammonium thiocyanate and rinse down the inside of the conical flask with a little distilled water. Complete the titration as quickly as possible by adding thiosulphate drop by drop with constant swirling of the mixture till with one drop the blue colour changes to white or faintly yellowish white. Take the burette reading and repeat the experiment with two other 25 ml. portions of the given copper solution.

Calculation

Let 25 ml. of given copper solution

$\equiv V$ ml. of $S(N)$ sodium thiosulphate solution

$=(V\times S)$ ml. of (*N*) sodium thiosulphate solution

$\equiv(V\times S)\times 0{\cdot}06357$ g. of Cu.

$\therefore$ Amount of copper per litre in the given copper-solution

$=V\times S\times 0{\cdot}06357\times 40$ g.

N.B. 1. Nitrous acid, oxides of nitrogen etc. interfere and hence they must be absent. And if they are present, they must be removed by boiling the given copper solution with urea.

2. Silver nitrate solution renders the end-point more sharp.

3. Too much dilution of the solution is to be avoided as far as practicable.

4. Some amount of iodine is adsorbed by cuprous iodide. Addition of ammonium thiocyanate converts Cu_2I_2 into $Cu_2(SCN)_2$, which is more insoluble; thus the adsorbed iodine is set free.

[Determination of total quantity contained in the sample supplied.

In all cases, to determine the total quantity contained in the sample, transfer the whole solution without loss into a cleansed 250 ml. volumetric flask. Rinse the bottle (in which the solution was supplied) several times with little distilled water and pour down the wash-water every time into the main solution in the volumetric flask. Make the solution up to the mark with distilled water. Put in a stopper and shake carefully so as to form a uniform solution. Measure out 25 ml. portion of this solution and carry out necessary operations as usual. Calculate the amount present in 25 ml. as usual and then multiply it by 10 to get the total amount contained in the sample supplied.]

CHAPTER V

TITRIMETRIC ANALYSIS OF SOME SPECIAL SAMPLES

Experiment

Determination of iron in iron wire

Weigh out accurately about 1 gm. of clean iron wire into a conical flask. Add about 25 ml. of dilute sulphuric acid and warm gently, if necessary. When the action* is complete (ignore any separation of carbon particles), cool the flask and transfer the contents without loss into a 250 ml. volumetric flask. Make up the volume to the mark with 2(N) H_2SO_4. Pipette out 25 ml., dilute to 50 ml., add 2 ml. syrupy phosphoric acid and titrate with standard $KMnO_4$ solution.

Alt. Method: Weigh out accurately about one gram of clean iron wire into a 500 ml. conical flask. To the weighed sample add 50 ml. of 1 : 1 HCl and place a short funnel in the neck of the flask. Warm gently and continue heating till the sample dissolves (ignore any separation of carbon particles). Rinse down the funnel and the neck of the flask with distilled water. Cool, filter through a quantitative filter paper into a 250 ml. volumetric flask. Wash with very dilute hydrochloric acid and collect the washings in the flask. Make up the volume to the mark.

Transfer 25 ml. of this solution into a conical flask and determine the iron titrimetrically say with standard $KMnO_4$ solution (see page 234) after reduction by stannous chloride. Carry out two further titrations at least and take the appropriate value for your calculations.

Calculations

Let the weight of the sample taken = W gms.

and 25 ml. of the iron solution

$$\equiv V \text{ ml. of } S\,(N)KMnO_4 \text{ solution}$$

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*If precision is desired, attach a Bunsen valve to the conical flask, when most of the iron has undergone dissolution. This device allows the hydrogen produced to escape but prevents the entry of air so that no oxidation can occur.

∴ Amount of iron in 25 ml. solution $=(V \times S \times 0{\cdot}056)$g.
Or, amount of iron in W gms. of the sample $=(V \times S \times 0{\cdot}056 \times 10)$g.
Hence the percentage of iron in the sample

$$= \frac{V \times S \times 0{\cdot}056 \times 10}{W} \times 100$$

Experiment

Determination of calcium in limestone

Weigh out accurately about 1.2 gm. of the powdered sample and take it in a 500 ml. beaker. Add 5 ml. of water and keep the beaker covered with cover glass. Now add in portions 10 ml. of conc. hydrochloric acid slowly and down the sides of the beaker. After the effervescence has ceased, heat on a water bath for a few minutes. Wash down the bottom of the cover and the inside of the beaker. Dilute to 50 ml. with water. Add 1-2 gms. of NH_4Cl and heat nearly to boiling. Add 5 drops of methyl orange and then 1 : 1 ammonia till faintly alkaline. Boil for 1-3 minutes and filter into a 250 ml. volumetric flask. Wash the residue, filter paper and beaker several times (after transferring the liquid) —First 3 or 4 times with hot water and then twice with hot 2% ammonium nitrate solution collecting all the washings in the flask. Cool the flask to room temperature. Add 5 ml. conc. HCl and make up the volume to the mark with distilled water.

Pipette out 25 ml. of the above solution in the beaker and dilute to 50 ml. Heat to about 90°. Add to this hot solution 50 ml. of a 4% ammonium oxalate solution almost in the boiling condition. Add 6N ammonia dropwise and slowly with constant stirring till the mixture is faintly alkaline. Complete or finish this within 5-10 minutes time. Allow to stand for half an hour (preferably one hour, if possible) on an asbestos board over a small flame.

Now follow the procedure as detailed in pp. 237-238 (from the 8th line from top of page 237).

Calculations

1 ml. of N $KMnO_4 \equiv 0{\cdot}020$g. of Calcium.
Let the weight of the sample taken = W gms.
strength of potassium permanganate = S(N) and
the volume of permanganate required = V ml.
Hence, the amount of calcium in Wg. of the mineral

$$= V \times S \times 0{\cdot}02 \times 10\text{g.}$$

∴ percentage of calcium in the mineral

$$=\frac{V\times S\times 0{\cdot}02\times 10}{W}\times 100$$

and percentage in terms of calcium oxide

$$=\frac{56}{40}\times\frac{V\times S\times 0{\cdot}02\times 10\times 100}{W}$$

Experiment

Determination of copper in copper wire (or brass, bronze)

Weigh out accurately about 1·5 gm. (1·5 to 2 gms in case of alloy) of copper wire in a 500 ml. beaker. Add 5 ml. water and 10 ml. conc. nitric acid down the sides of the beaker and keep the beaker covered with a cover glass. As soon as the reaction slackens down, heat on water bath to hasten the reaction and finally ensure complete dissolution of the sample. When the reaction is complete† (the sample gets dissolved), wash down the inner side of both cover glass and beaker with about 25 ml. of water. Add 1—2 gms. of urea and boil for a few minutes to remove nitrous fumes (nitrous acid and oxides of nitrogen). Cool the mixture. Transfer the liquid quantitatively into a 250 ml. volumetric flask and make up the volume to the mark.

Pipette out 25 ml. of the solution into a conical flask and dilute to 50 ml. Neutralise with minimum amount of 1 : 1 NH_4OH, boiling off the excess of it. Add 2 gms of NH_4HF_2* followed by 2 gms. of KI. Titrate using starch as indicator by running in standard solution of thiosulphate from a burette. Repeat the experiment with two other 25 ml. portions of the solution.

Calculations

Let the weight of the sample (alloy or wire) taken = W gms.
25 ml. of the solution ≡ V ml. of S(*N*) thiosulphate solution.
Since 1 ml. of (*N*) sodium thiosulphate solution
≡ 0·06357 gm. of copper,
(V × S) ml. of (*N*) thiosulphate solution
≡ (0·06357 × V × S) g. of Copper

∴ percentage of copper in the sample

$$=\frac{0{\cdot}06357\times V\times S\times 10}{W}\times 100$$

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†In case of brass and bronze better results are obtained by fuming with conc. H_2SO_4.

*In case of copper wire 5 ml. glacial acetic acid may be used instead of bifluoride.

CHAPTER VI

GRAVIMETRIC ESTIMATION

Experiment

Estimation of Iron as Ferric oxide

Principle

When the solution containing ferric salt is treated with a slight excess of ammonium hydroxide solution, ferric hydroxide is precipitated:

$$FeCl_3+3NH_4OH=Fe(OH)_3+3NH_4Cl$$

Ferric hydroxide on ignition yields ferric oxide.

$$2Fe(OH)_3=Fe_2O_3+3H_2O$$

From the weight of this ignited residue the amount of the element is calculated.

Procedure

Transfer the solution into a 500 ml. beaker without loss and rinse down the bottle that contained the solution several times with distilled water into the same beaker. Dilute with distilled water to about 50 ml. Add 10 ml. of 1 : 1 hydrochloric acid, 1-2 ml. conc. HNO_3 and boil gently the mixture till the colour is yellow. Dilute the solution to about 200 ml. with distilled water. Add 2 gms. of NH_4Cl, heat the solution to boiling, add a slight excess of pure 1 : 1 ammonium hydroxide solution slowly and with constant stirring (indicated by the faint smell of ammonia). Heat gently so as to boil for a minute or two and allow the precipitate to stand for some time. When the precipitate settles down, decant the supernatant liquid (which should be colourless) without disturbing the precipitate through an ashless quantitative filter paper (Whatman No. 41). Add about 100 ml. of boiling 1% ammonium nitrate solution to the ppt., stir and allow to settle. Decant the supernatant liquid into the filter as before. Repeat this process of washing 3 to 4 times and then transfer the ppt. on to the filter without loss. Dislodge the last traces that may adhere to the side of the beaker with the help of 'Policeman' and finally transfer by a jet of hot water from a wash bottle down into the filter. Wash the ppt. on the filter paper with hot and very dilute (1% soln.) ammonium nitrate solution. Continue washing till a few drops of last washings, when poured into $AgNO_3$ solution acidified with dil. HNO_3 fail to produce any opalescence. Allow each portion of the wash liquid to run through before adding the next. While the filtration is in progress, heat a clean porcelain or silica crucible at red heat, cool in a desiccator for half an hour and weigh. Repeat the process of heating, cooling and weighing till a constant weight is obtained.

When the filter paper has drained thoroughly, carefully take it off, fold the paper around the ppt. and place it in the weighed crucible. Heat very gently at first over a small flame taking care that the paper only chars but does not lit up. Burn off the carbon with free access of air. Put the lid on covering three-fourths of the crucible so as to exclude the flame gases from interior of the crucible and ignite the ppt. at a red heat for about 15 minutes. Cool in a desiccator for about 30 minutes and weigh. Repeat the process of heating, cooling and weighing till the weight of the crucible becomes constant.

Calculation

Let the weight of the empty crucible $= W_1$ gms. and the weight of (crucible$+Fe_2O_3$)$=W_2$ gms.

$\therefore$ Weight of $Fe_2O_3=(W_2-W_1)$ gms.

For every gm. of Fe_2O_3, there is 0·6994 gm. of Fe

$\therefore$ amount of Fe in the solution$=(W_1—W_2)\times 0{\cdot}6994$ gms.

N.B. (*i*) This method of analysis cannot be adopted in presence of other elements; such as aluminium, chromium, etc. that are precipitated by ammonium hydroxide.

(*ii*) The solution with the ppt. should not be heated for a long time, as this may break up the aggregates and cause the ppt. to become slimy or even colloidal.

(*iii*) Heating of the ppt. should be carried out under good oxidising condition, as otherwise partial reduction may occur. Besides, heating of the ppt. $Fe(OH)_3$ at a temperature higher than 1,000°C may lead to the formation of tri-ferric tetroxide. In either case, the results is affected.

(*iv*) In accurate work *double precipitation* method should be followed as this minimises error due to *co-precipitation*.

(*v*) A glass rod with a rubber tubing attached to one end of it is known as policeman.

Experiment

Estimation of silver as silver chloride

Principle

If to a solution of silver salt acidified with dil. HNO_3, dil. hydrochloric acid be added AgCl is precipitated.

$$AgNO_3 + HCl = \dot{A}gCl + HNO_3.$$

From the weight of the washed and dried AgCl, the amount of silver is calculated.

Procedure

Transfer the solution into a 400 ml. beaker without loss and rinse down the bottle that contained the solution several times with distilled water into the same beaker. Dilute to 100 ml. and add a little of dil. HNO_3. (Note that the solution should contain 0·1 g. of silver per 200 ml. and 1% by volume of nitric acid.) Heat the mixture to about 70°C and add dil. HCl (approximately 0·2*N*) dropwise with constant stirring till the precipitation is complete, but *don't add* a large excess of acid. Warm till the ppt. settles down; then allow to stand and when it cools down to room temperature add a few drops of dil. HCl to the supernatant liquid. Absence of any turbidity at this stage indicates that the precipitation is complete. Cover the beaker with a clock glass and allow it to stand in a dark place for about half an hour or longer (preferably, one night). Now determine the constant weight of the *Gooch crucible* (no. 3) dried at 135°C. Pour down the supernatant liquid through the weighed *Gooch* retaining as much ppt. in the beaker as possible. Cover the ppt. in the beaker with 0·1 (*N*) nitric acid. Stir, allow to settle and decant the supernatant liquid through the *Gooch crucible*. Repeat this process of washing by decantation for several times and finally transfer the ppt. to the crucible without loss. Wash the ppt. several times with 0·01(*N*) nitric acid till the wash-liquid gives no opalescence with $AgNO_3$ solution acidified with dil. HNO_3. (This indicates that the ppt. is free from chloride.) Dry the washed ppt. first, at 100°C and then at 130°—150°C in an air oven. Cool in a desiccator and weigh as AgCl. Repeat the process of heating, cooling and weighing till the weight becomes constant.

Calculation

Let the weight of the empty crucible $= W_1$ gms. and the weight of the crucible $+$ AgCl $= W_2$ gms.

$\therefore$ weight of AgCl $= (W_2 - W_1)$ gms.

For every gm. of AgCl there is 0·7526 g. of silver.

$\therefore$ amount of silver $= (W_2 - W_1) \times 0{\cdot}7526$ gms.

N.B. (*i*) Silver chloride undergoes considerable decomposition in bright light and hence the error due to decomposition is minimised by carrying out the experiment in as subdued a light as possible.

(*ii*) Washing with simple water may render the silver chloride colloidal in nature. The wash solution, therefore, must contain an electrolyte to prevent it and HNO_3 is generally used for this purpose.

Experiment

Estimation of sulphate (in a soluble sulphate) as Barium sulphate.

Principle

If to a hot solution of sulphate made slightly acidic with hydrochloric acid, a dil. solution of barium chloride is slowly added with constant stirring, barium sulphate is quantitatively precipitated.

$$Ba^{++} + SO_4'' = BaSO_4.$$

From the weight of barium sulphate, the amount of sulphate is calculated.

Procedure

Transfer the solution without loss into a 400 ml. beaker and rinse down the bottle that contained the solution several times with distilled water into the same beaker. Add about 0·5 ml. conc. HCl and dilute the solution to about 250 ml. Heat the solution to boiling. To this hot solution add drop by drop a 5% solution of barium chloride (during addition stir constantly the solution in the beaker) till the precipitation is complete. Allow the ppt. to settle for a minute or two. To test complete precipitation, add a drop or two of barium chloride solution to the supernatant liquid. If any ppt., continue addition of barium chloride solution in the manner indicated above and test again for complete precipitation. (A little excess of the precipitant must be present.) Cover the beaker with a clock glass. Keep the solution hot for half an hour (preferably one hour) by placing it on an asbestos board over a small flame. Take care that the total volume of the solution does not fall below 200 ml. Determine the constant weight of the porcelain crucible, while the heating of the mixture over a low flame is going on. Stop heating; rinse down the under side of the clock glass covering the beaker and remove the clock glass. Decant the supernatant liquid through a quantitative filter paper of negligible ash content (Whatman—No. 40 or No. 540). Cover the ppt. in the beaker with water and filter by decantation. Repeat the process several times and transfer the ppt. completely onto the filter. Dislodge the ppt. that adheres to the walls of the beaker by rubbing with a glass rod and then transfer into the filter by a jet of water directed from wash bottle into the beaker. Wash the ppt. with small portions of hot water by directing the jet as near to the top of the filter as possible. Allow each portion of wash liquid to be completely drained off before adding the next. Repeat the process till the wash liquid is free from chloride. (Test as usual with $AgNO_3$ solution.).

Take out the filter paper carefully, fold it around the ppt. and place it in a porcelain crucible, the constant weight of which is previously determined. Cover the crucible loosely with its lid and dry the filter paper by heating gently over a very low flame. Now increase the size of the flame taking care that the paper only chars but does not take fire. When the charring is complete, place the crucible in a slightly inclined position with cover displaced a little and heat to dull redness. When all the carbon is burnt off and the contents become white, heat the crucible at red heat for 15 minutes. Allow the crucible to cool somewhat in the air, then cool in a desiccator and when it cools down to laboratory temperature, take it out and weigh. Repeat the process of heating for ten minutes followed by cooling and weighing till the weight becomes constant.

Calculation

Let the weight of empty crucible$=W_1$ gms. and the weight of crucible$+BaSO_4=W_2$ gms.

$\therefore$ Weight of $BaSO_4=(W_2-W_1)$ gms.

But for every gm. of $BaSO_4$, there is 0·4115 gm. of SO_4''

$\therefore$ amount of $SO_4''=(W_2-W_1)\times 0{\cdot}4115$ g.

N.B. (*i*) To prevent the precipitation of other anions, such as carbonate, chromate, phosphate, etc., the precipitation is carried out in slightly acid solution.

(*ii*) In order to have the ppt. of filterable size, precipitation is carried out in hot solution. Slow addition of $BaCl_2$ to hot solution with constant stirring minimises also the errors due to co-precipitation.

(*iii*) Reduction of $BaSO_4$ to BaS is avoided first by charring the paper without inflaming and then by burning off the carbon with free access of air.

[Re: Procedure in a gravimetric analysis

In absence of any special direction, follow the procedure already described. If dilution (which depends on concentration of the solution supplied) of the given solution up to an exact volume becomes imperative, transfer without loss the solution into a volumetric flask of definite volume (as directed). Rinse down several times the bottle that contained the solution with distilled water into the flask. Shake carefully. Make the volume up to the mark with distilled water. Put in a stopper and shake well to have a uniform solution. Pipette out 25 ml. or 50 ml. (or, as directed) portion of the solution and carry out the experiment as usual. Perform two experiments (pipetting out equal volume each time) side by side (or as directed)].

PART IV

QUANTITATIVE ORGANIC ANALYSIS

Experiment

Estimation of Formaldehyde

Theory

Formaldehyde is oxidised quantitatively to formic acid by iodine in excess alkali. The oxidation is actually caused by hypoiodite ion resulting from the reaction between iodine and alkali. Excess alkali neutralises the formic acid thus formed.

$$I_2+2NaOH=NaI+NaOI+H_2O \quad \ldots \quad (i)$$

$$HCHO+NaOI=HCOOH+NaI \quad \ldots \quad (ii)$$

$$HCOOH+NaOH=HCOONa+H_2O$$

On adding, $HCHO+I_2+3NaOH=HCOONa+2NaI+2H_2O \quad \ldots \quad (iii)$

On completion of oxidation of formaldehyde the reaction mixture is acidified, when the hypoiodite left over oxidises the iodide present in the mixture [cf. eqns. (*i*) & (*ii*)] leading to liberation of iodine : $OI'+I'+2H^+ \longrightarrow I_2+H_2O$.

Iodine thus liberated is titrated with a standard thio:

$$I_2+2S_2O_3''=S_4O_6''+2I'.$$

Knowing the volume of thiosulphate equivalent to the iodine consumed by formaldehyde the amount of the latter can be calculated.

From the equation (*iii*) given above:

1 gm-mole of iodine ≡ 1 gm-mole of formaldehyde

or, 2 litres of (N) iodine ≡ 30 gms. of formaldehyde

or, 1 ml. of 0·1(N) iodine ≡ 1 ml. of 0·1(N) thio $\equiv \dfrac{30}{2000\times 10}$ g.

$=0{\cdot}0015$ g. of formaldehyde.

Dilution of formalin solution: Measure out 5 ml. formalin into a litre flask about half filled with distilled water, mix well and make up the volume to the mark. (The solution is thus 0·2% approx).

Preparation of 0·1(*N*) *iodine Solution*: Iodine is reduced to iodide; $I_2+2e=2I'$. Hence the equivalent weight of iodine is the same as its atomic weight, which is 126.92. To prepare 1 litre of 0·1(N) solution, therefore, requires 12·69 gms. of iodine.

Take in a glass stoppered flask of 1-litre capacity about 20 gms, of iodate free potassium iodide and dissolve in 30-40 ml. of water. Weigh out on a rough balance about 12·7 gms. of A. R. quality iodine and pour it into the above concentrated solution of potassium iodide with the help of a clean and dry small funnel fitted on to the flask. Remove the funnel, put in the glass-stopper and shake in the cold till the whole of iodine goes into solution. Leave the solution to attain room temperature and then make up the volume to the mark with distilled water. Keep it stoppered in a cool and dark place.

Procedure

Take a 25 ml. portion of a dilute solution (0·2% approx) of the aldehyde in a 250 ml. flask. Mix 50 ml. of about N/10 iodine with it. Add gradually and dropwise avoiding excess a 5% solution of NaOH till the liquid turns light brown, fading to a very pale yellow colour, which persists even when allowed to stand for quarter of an hour. Leave the solution to stand for about 10-15 minutes. Now acidify the solution by adding 15 ml. of 5% HCl. Titrate the liberated iodine with a standard solution of thiosulphate using starch as indicator.

Titrate again with the standard solution of thiosulphate a 25 ml. portion of the iodine solution taken in a 250 ml. flask and diluted to about 100 ml. using starch as indicator. Deduce the net volume of thiosulphate equivalent to the iodine consumed by formaldehyde.

Calculations

Let the strength of thiosulphate solution = S $(N/10)$ and the volume of thiosulphate required to titrate 25 ml. of $0{\cdot}1(N)$ iodine solution $= v_1$ ml.

$\therefore$ Volume of thiosulphate required to titrate 50 ml. of $0{\cdot}1(N)$ iodine solution $= 2v_1$ ml.

Again suppose the volume of thiosulphate required to titrate the liberated iodine (i.e., excess iodine in a mixture of 25 ml. of the aldehyde + 50 ml. of $N/10$ iodine) $= v_2$ ml.

$\therefore$ Volume of thiosulphate equivalent to the iodine consumed by 25 ml. of the dilute solution of aldehyde $= (2v_1 - v_2)$ ml.

Or, amount of formaldehyde in 25 ml. of diluted solution $= (2v_1 - v_2) \times 0.0015 \times \text{S}$g.

$\therefore$ amount of formaldehyde in gms/litre

$$= \frac{(2v_1 - v_2) \times 0.0015 \times S}{25} \times 1000 \text{ g.}$$

$$= (2v_1 - v_2) \times 0{\cdot}06 \times S \text{ g.}$$

N.B.—1. Excess alkali should always be avoided.

2. To determine the total amount of formaldehyde transfer without loss the supplied solution (see page 246) to a 250 ml. volumetric flask and make up the volume with water. Carry out your expt. by measuring out a 25 ml. or any suitable volume (as directed) of the diluted solution. Calculate as usual the amount present in this volume and multiply it by 250/x (where x = volume in ml. of the dilute solution taken for experiment) to get the total amount contained in the supplied sample.

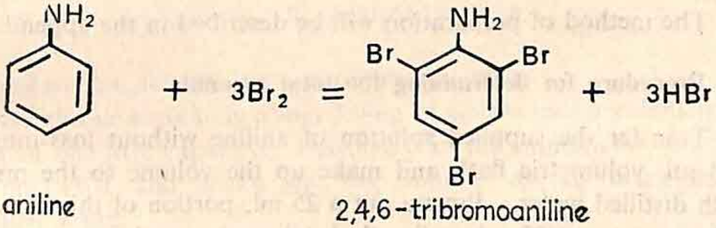
Experiment

Determination of Aniline by bromination

Theory

Aniline on treatment with an excess of bromate-bromide solution in presence of hydrochloric acid undergoes quantitative bromination by the bromine liberated from the reaction between bromate and bromide in the acid medium, when a precipitate of 2, 4, 6-tribromoaniline is obtained. Hence, the use of the reaction in the estimation of aniline.

$$KBrO_3+5KBr+6HCl=3Br_2+6KCl+3H_2O$$



The excess bromine is determined by adding KI in excess and titrating the liberated iodine with a standard thiosulphate solution using starch as an indicator.

$$Br_2+2KI=I_2+2KBr$$
$$I_2+2Na_2S_2O_3=Na_2S_4O_6+2NaI$$

We can, therefore, write from the above equations :

$$1C_6H_5NH_2\equiv 3Br_2\equiv 3I_2\equiv 6Na_2S_2O_3$$

Hence, 1ml. of N/10 $Na_2S_2O_3\equiv 0{\cdot}001552$g. (Molecular weight of aniline being 93·12).

Reagents required

(*i*) Potassium bromate-bromide solution of 0·1N order, (*ii*) sodium thiosulphate solution of 0.1N order, (*iii*) 20% potassium iodide solution and (*iv*) starch solution.

The experiment involves:

Preparation of bromate-bromide solution of 0.1*N order*.

Weigh out accurately about 0·6-0·8g. of A. R. quality $KBrO_3$ and about 10g. of A. R. quality KBr in a 250 ml. volumetric flask. Dissolve it in water and make up the volume to the mark.

Suppose the weight of bromate taken=W g.

Hence, the strength of the solution = W/0.6959 N/10 [Equivalent wt. of $KBrO_3$ as an oxidising agent being 1/6 Mol. wt.]

Preparation of thiosulphate solution of 0.1*N order.*

This has already been discribed on page 241.

Preparation of 20% *KI solution*

Dissolve 100 gms. of A.R. KI in water in a bottle and dilute to 500 ml.

Preparation of starch solution

The method of preparation will be described in the appendix.

Procedure for determining the total amount

Transfer the supplied solution of aniline without loss into a 250 ml. volumetric flask and make up the volume to the mark with distilled water. Pipette out a 25 ml. portion of this diluted solution into a 500 ml. iodine flask (glass stopper bottle)*. Add 50 ml. $KBrO_3$—KBr solution followed by 5 ml. conc. HCl and stopper the flask immediately. Shake the flask for a minute to mix the reactants thoroughly. Allow the flask to stand at room temperature for about 15 minutes giving it a swirling motion from time to time. Add 10 ml. of 20% KI solution. Stopper the flask, shake for a minute and again allow to stand for about ten minutes at room temperature. Take off the stopper, wash it and the neck of the flask with little distilled water taking care that no wash liquid falls outside the flask. Titrate the liberated iodine with standard thiosulphate solution adding 2ml. of starch as indicator as close to the end point as possible. Carry out at least two further titrations exactly in the same way with two other 25 ml. portions of the diluted solution of aniline. Take the mean of the readings.

Standardise the thiosulphate solution with the bromate-bromide solution using 25 ml. of the latter for each titration.

Results

The mean volume of thiosulphate required for 25 ml. of bromate-bromide solution in the standardisation $= v_1$ ml.

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*In absence of it use conical flask and watch glass.

∴ the volume of thiosulphate required for 50ml. of bromate-bromide solution in the standardisation$=2v_1$ ml.

The mean volume of thiosulphate solution required for 50 ml. of bromate-bromide solution in the determination$=v_2$ ml.

Calculation

Let the strength of thiosulphate solution=S (N/10).

Volume of thiosulphate equivalent to bromine consumed by aniline$=(2v_1-v_2)$ ml.

∴ amount of aniline in 25 ml. diluted solution.

$$=\{(2v_1-v_2)\ S\times0{\cdot}001552\}\ \text{g}$$

Hence, the total amount of aniline supplied

$$=\{(2v_1-v_2)\ S\times0{\cdot}001552\times10\}\ \text{g}.$$

Procedure for determining the percentage purity

Weigh out accurately about 1·0gm of aniline into a volumetric flask of one litre capacity. Dissolve it in the minimum volume of dil. HCl and make up the volume to the mark with distilled water.

Pipette out a 25 ml. portion of this prepared solution and carry out the experiment under exactly the same terms and conditions as stated before, Repeat the experiment at least twice and take the mean of the readings for your calculation. Standardise the thiosulphate solution as before taking 25 ml. of bromate-bromide solution.

Results

The mean volume of thiosuplhate solution required for 25 ml. of bromate-bromide solution in the standardisation$=v_1$ ml.

∴ volume of thiosulphate required for 50 ml. of bromate-bromide solution in the standardisation$=2v_1$ ml.

The mean volume of thiosulphate solution required for 50ml. of bromate-bromide solution in the determination$=v_2$ ml.

Amount of aniline weighed out$=w$ g.

Calculation

Let the strength of thiosulphate solution=S (*N/10*).

Volume of thiosulphate equivalent to bromine consumed by aniline$=(2v_1-v_2)$ml.

∴ amount of aniline in 25 ml. of the prepared solution

$$=\{(2v_1-v_2)\times S\times0{\cdot}001552\}\ \text{g}.$$

or amount of aniline in one litre of the prepared solution

$= \{(2v_1 - v_2) \times S \times 0{\cdot}001552 \times 4 \times 10\}$ g.

$\therefore$ the percentage purity of aniline

$$= \frac{(2v_1 - v_2) \times S \times 0.001552 \times 4 \times 10}{w} \times 100$$

$$= \frac{(2v_1 - v_2) \times 6{\cdot}2}{w}$$

N.B. The method works well at a low concentration (about 0.1%) of aniline.

Experiment

Determination of glucose with Fehling's solution

Theory

Glucose reduces (cupric ions of) Fehling's solution to red cuprous oxide. Knowing the concentration of glucose solution the weight of glucose equivalent to 1 ml. of Fehling's solution can be calculated.

Hence, we can determine an unknown glucose solution by a glucose solution of known concentration by titrating against a common Fehling's solution (i.e., comparison solution).

The experiment therefore involves:

(*i*) Preparation of a standard solution of glucose.

(*ii*) Titration of a Fehling's solution with the standard glucose solution, i.e., standardisation of the Fehling's solution supplied.

(*iii*) Titration of the Fehling's thus standardised with the given glucose solution of unknown concentration.

Procedure

(*i*) *Preparation of a standard glucose solution* : Take in a 250 ml. volumetric flask about 1·25 g. of A. R. quality glucose by weighing accurately in a chemical balance and make up the volume to the mark.

(*ii*) *Standardisation of the Fehling's solution*

Take in a 250 ml. conical flask 20 or 50 ml. of Fehling's solution* as follows: Transfer a 10 or 25 ml. portion of solution A to the conical flask and mix with it an exactly equal volume of solution B.

Now heat the solution to gentle ebullition on an asbestos centred wire-gauze; add 2 drops of methylene blue[1] indicator and without removing the flame run in from a burette the standard glucose solution till the blue colour of the solution vanishes and suddenly a bright red ppt. settles down at a time. This indicates an approximate titre value and will act as a guide for subsequent titrations. To have a fairly accurate value repeat the titration by adding methylene blue indicator near the end-point of the reduction. Run in, all at a time, almost an equal volume of glucose solution consumed in the previous rough titration to a fresh solution of Fehling taken in the flask as only 0·5—1 ml. of the glucose solution will be necessary to finish the titration. *Keep the solution gently boiling all the time* during the process. Don't remove the flame, add 2-3 drops of indicator to the boiling solution. Now quickly finish (i.e., within one minute more) the titration by dropwise addition of glucose solution taking care that the boiling does not come to a stop. Repeat the titrations to obtain a conformable value, values which must not differ by more than 0.1 ml.

Take the mean value and calculate the weight of glucose equivalent to 1 ml. of Fehling's solution.

(*iii*) *Titration of standardised Fehling's with the glucose solution of unknown concentration*:

Wash the burette thoroughly with distilled water and then rinse it at least twice with the glucose solution of unknown concentration. Fill the burette with the glucose solution. Take 20 or 50 ml. portion of the Fehling's solution in a conical flask and titrate exactly in the same way as before by running in the unknown glucose solution taken in the burette.

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*Preparation of Fehling's solution : Prepare as follows the Fehling's solution required for the purpose.

Solution A. Dissolve 34·64 g. of A. R. quality of crystallised copper sulphate $CuSO_4.5H_2O$ in water and make up the volume roughly to 500 ml. in a bottle.

Solution B. Dissolve 50 g. of pure caustic soda in water and 173g. of Rochelle salt in warm water. Mix the two solutions—the alkali and the tartrate. Cool and make up the volume roughly to 500 ml. in a bottle. Keep the solutions A & B well stoppered.

[1] Dissolve 0·5g. in 100 ml. distilled water.

Repeat the titrations, tabulate the results as usual and take the mean value for your calculations.

Results

Table 1

Weight of glucose

First weight	Second weight	Difference in weight, i.e., the weight of glucose taken.
W_1 gms.	W_2 gms.	(W_1-W_2) gms. i.e., say w gms.

Table 2

Standardisation of Fehling's solution

No. of observations	Total volume (A+B) of Fehling's solution in ml.	Burette reading in ml.		Vol. of glucose solution consumed in ml. =Final−initial	Mean vol. of glucose solution consumed
		Initial	Final		
1	x				Say y ml.
2	x				
3	x				

Table 3

Standardised Fehling's soln. vs. Unknown glucose

No. of observations	Total volume (A+B) of Fehling's solution in ml.	Burette reading in ml.		Vol. of glucose solution consumed in ml. =Final—initial	Mean vol. of glucose solution consumed
		Initial	Final		
1	x′				Say z ml.
2	x′				
3	x′				

Calculations

The weight of glucose present in 250 ml. $=w$ gms.

x ml. of Fehling's $\equiv y$ ml. of known glucose solution.

x' ml. of Fehling's $\equiv z$ ml. of unknown glucose solution.

$\therefore$ 1 ml. of Fehling's $\equiv y/x$ ml. of known glucose solution.

$$=\frac{w}{250}\times\frac{y}{x}\cdot \text{ gms. of glucose.}$$

or x' ml. of Fehling's $\cong \frac{w \times y \times x'}{250 \times x}$ gms. of glucose.

$\therefore$ amount of glucose in gms/litre in the supplied (unknown) solution $= \frac{w \times y \times x'}{250 \times x \times z} \times 1000 = \frac{w \times y \times x' \times 4}{x \times z}$

When $x = x'$ i.e., when identical volumes of Fehling's are taken for both sets of titrations, the above expression becomes $w \times y/z \times 4$.

N.B. 1. Standardisation and titration (with unknown glucose) should be carried out under identical conditions as far as practicable.

2. To give a little swirling motion to the flask may prove helpful for sharp indication of the end point, which otherwise might escape unnoticed due to the side-colour.

3. The indicator solution should preferably be a freshly prepared one.

4. To determine the total amount of glucose transfer the supplied solution without loss (see page 246) to a 250 ml. volumetric flask and make up the volume with water. Titrate as usual the standardised Fehling with this glucose solution taken in a burette.

Total amount in the sample supplied $= \frac{w \times y \times x'}{250 \times x \times z} \times 250$ gms.

$$= \frac{w \times y \times x'}{x \times z} \text{ gms.}$$

$$= (w \times y/z) \text{ gms., when } x = x'.$$

PART V

PREPARATION OF ORGANIC COMPOUNDS

1. Iodoform, CHI_3 from ethyl alcohol.

5 gms. (6·5 ml.) ethyl alcohol
15 gms. sodium carbonate in 50 ml. water.
10 gms. powdered iodine.

Take the sodium carbonate solution in a 100 ml. beaker and add ethyl alcohol to it. Now add the powdered iodine in small quantities at a time with constant stirring so as to dissolve it in the above mixture. Warm the mixture to 60-80°C. [The mixture turns pale yellow and yellow crystals of iodoform separate out on cooling.] Allow it to cool and filter at the suction. Wash well using small quantities of distilled water at a time. Recrystallise, if necessary, from rectified spirit, dry and determine the m.p. It melts at 119° and sublimes. The yield of crude product is about 0·8 gm.

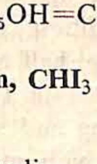
$$4I_2+6NaOH+C_2H_5OH=CHI_3+HCOONa+5NaI+5H_2O$$

Iodoform, CHI_3 from acetone

1 ml. acetone
7 gms. powdered iodine
3 gms. caustic soda in 250 ml. water.

Mix acetone with the caustic soda solution in a 600 ml. beaker and now add iodine to it in small quantities at a time with constant stirring till the whole of iodine dissolves in the mixture. Allow it to stand for fifteen minutes, filter, wash and recrystallise as before, if necessary. Dry and determine the m.p. The yield of the crude product is about 1.7 gm.

2. Sulphanilic acid



$(NH_3^+ C_6H_4SO_3^-)$

12.5 gms. aniline
40 gms. conc. sulphuric acid.

Mix aniline and conc. sulphuric acid cautiously in 100 ml. round flask. Heat the contents of the flask in an oil bath or metal bath to 180°-190° till no aniline separates out on addition of exeess of NaOH to a little of the sample dissolved in water. This requires heating for four to five hours. Pour the contents of the flask into cold water, when sulphanilic acid is precipitated out as a grey crystalline mass. Filter, wash with a little cold water and recrystallise from hot water with the addition of a little animal charcoal. Dry in air. Yield 13—15 gms. The substance decomposes on heating before melting.

$C_6H_5NH_2+H_2SO_4=NH_3^+C_6H_4SO_3^-+H_2O.$

3. **Acetanilide** $C_6H_5NHCOCH_3$

Method I : 4 ml. aniline
6·5 ml. acetic anhydride

Heat 80 ml. water just to boil in a 250 ml. conical flask. Remove the source of heat and add 4 ml. aniline with shaking. Place the flask on a boiling water bath. Pour into the clean and uniform solution 6·5 ml. of acetic anhydride in three or four almost equal instalments (or add, if possible slowly and dropwise with the help of a dropper) with shaking, completing the operation in half an hour. When the addition is over continue heating in the same way for an additional half an hour with occasional shaking. Now allow the contents of the flask to cool down to room temperature with shaking and scratching from time to time. Filter at the pump, wash with minimum volume of cold water, drain well and dry.

White shining plate like crystals, m.p.* 114°C; yield about 4 gms.

Method II : 10 ml. aniline
9·2 ml. conc. HCl.
12·8 ml. redistilled acetic anhydride
16·5 gm. sodium acetate in 50 ml. of water.

Take 250 ml. water in a 500 ml. beaker, add conc. hydrochloric acid, pour in aniline and stir till a homogeneous mixture is obtained. Now add acetic anhydride to the above mixture. Stir till it passes completely into solution and immediately add sodium acetate solution. Stir vigorously and cool in ice. Filter at the suction, wash the acetanilide with a little water and allow it to drain. Dry in air on filter paper. The substance melts at 113°. Yield is about 12g.

It may be recrystallised from 250 ml. of boiling water containing 5 ml. of methylated spirit. Melting point of recrystallised product is 114°.

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*Recrystallise, if necessary from about 100 ml. of boiling water containing 2 ml. methylated spirit.

4. p-Bromoacetanilide, $BrC_6H_4NHCOCH_3$

5 gms. acetanilide
2 ml. bromine
25 ml. glacial acetic acid.

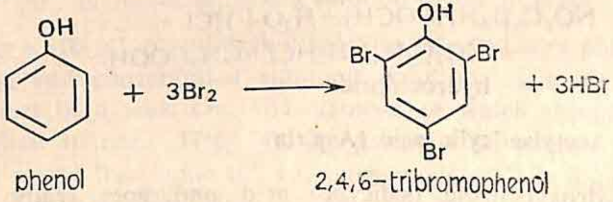
Dissolve bromine in about twice its volume of glacial acetic acid. Take a 500 ml. conical flask and dissolve acetanilide in acetic acid in this flask. Now add gradually the solution of bromine to acetanilide solution. When the whole of bromine has been added, allow the mixture to stand for 15 minutes and pour the contents of the flask into a beaker containing 200 ml. water. (Rinse out the flask well with water.) A crystalline ppt. will be obtained. Filter at the pump and wash with water the residue on the filter three or four times. Press it down and allow it to drain. Crystallise the substance from spirit by dissolving it in 60 ml. spirit taken in a beaker. Filter, wash again with a little dilute spirit, dry on filter paper or preferably on porous earthenware and determine the melting point. The substance melts at 165-66°. Yield is about 6-7 gms.

$$C_6H_5NHCOCH_3+Br_2=BrC_6H_4NHCOCH_3+HBr.$$

5. Tribromophenol

3 gms. phenol
Bromine water or a solution of
bromine in glacial acetic acid.

Phenol readily reacts with bromine to give an immediate white precipitate of 2, 4, 6-triobromophenol.



Dissolve 3 gms. of phenol in about 40 ml. of water in a 100 ml. conical flask. Add a strong aqueous bromine dropwise with constant stirring till a pale yellow colour persists. Warm the mixture on a water bath for a few minutes. Cool and then pour into 100 ml. water taken in a beaker. Filter at the pump and wash the residue, the desired bromo compound on the filter with a little of cold water. Dry and determine the melting point.

The yield is theoretical and the m.p. is 95°C.

6. p-Nitracetanilide $NO_2C_6H_4NHCOCH_3$.

12 gms. acetanilide
12 ml. glacial acetic acid
25 ml. conc. sulphuric acid
5 ml. fuming nitric acid.

Mix in a 250 ml. beaker acetanilide, acetic acid and sulphuric acid by stirring. Cool in a freezing mixture. Now add HNO_3 slowly and gradually at such a rate that the temperature does not rise above 20°. When the whole of nitric acid has been added, stir the mixture for an hour and pour on to ice. Dilute with water, let stand for some time. Filter, wash and dry on porous plate. Recrystallise from dilute alcohol, if necessary. M.p. of the substance is 207°. Yield is about 80% of the theoretical.

$$C_6H_5NHCOCH_3+HNO_3=NO_2C_6H_4NHCOCH_3+H_2O.$$

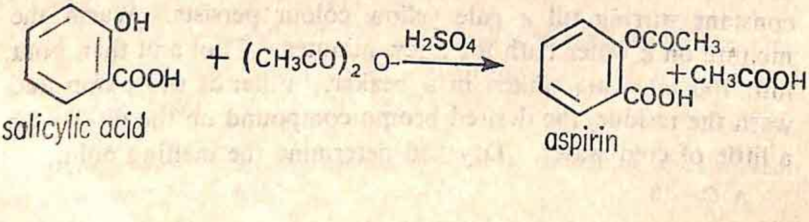
7. p-Nitraniline, $NO_2C_6H_4NH_2$

Either boil the above nitracetanilide with about 2½ times its weight of conc. HCl or heat it on water-bath with twice its weight of sulphuric acid, which is a mixture of equal volumes of sulphuric acid and water, until the liquid remains clear on dilution with water. Now dilute the liquid with water and precipitate the nitraniline by adding an excess of ammonia or caustic soda solution. Cool, filter the yellow crystalline ppt., wash and recrystallise from boiling water. Dry and determine the melting point. It melts at 147°. Yield is about 12 gms.

$$NO_2C_6H_4NHCOCH_3+H_2O+HCl$$
$$=\underset{\text{hydrochloride}}{NO_2C_6H_4NH_2HCl}+CH_3COOH$$

8. Acetylsalicylic acid (Aspirin)

o-Hydroxybenzoic (salicylic) acid undergoes ready acetylation with acetic anhydride in presence of a little conc. sulphuric acid acting as a catalyst.



Procedure

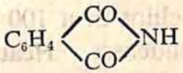
Take in a small conical flask 10 g. of dry salicylic acid, 14 ml. of acetic anhydride, 5 drops of conc. sulphuric acid and give the flask a whirling motion to have a thorough mixing. Warm on a water bath at 50-60° for about 1/4th. of an hour and stir with the thermometer during the process. Now allow the mixture to cool with occasional stirring. Dilute with 150 ml. of water, stir well and finally filter at the pump. Purify the crude by recrystallisation from a mixture of equal volumes of water and acetic acid.

Alternative method of purification:

Dissolve the crude in about 30 ml. of hot alcohol and pour the resulting solution into about 75 ml. of warm water. If any solid separates here, warm to secure complete solution. Now allow the clear solution to cool slowly, when lovely needle-shaped crystals separate out.

The yield is 13 gms. It has no sharp melting point, decomposition ranges in between 128° and 135°.

9. Phthalimide



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$$

10 gms. phthalic anydride

10·5 ml. conc. ammonia solution of sp. gr. 0·88.

Mix in a 100 ml. round flask fitted with air condenser phthalic anhydride and concentrated ammonia solution. The air condenser must be a wide one, the diameter of which should not be less than 10 mm. Heat first by placing over a wire gauze and then over a free flame till a homogeneous melt is obtained. Give the flask occasional shaking and push down the sublimate, if any, from inside the condenser with the help of a glass rod into the flask. Pour the contents whilst still hot into a prorcelain basin. Let it cool and reduce the product into fine powder by grinding in a mortar. The substance melts at 233—234°. Yield is about 9·5 gms. Recrystallise from alcohol, if necessary.

Alt. Method

20 gms. phthalic anhydride
4 gms. urea

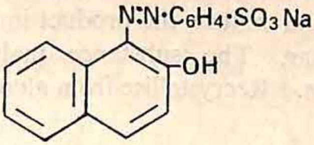
Mix urea and pure phthalic anhydride thoroughly and take the mixture in a round bottomed 500 ml. long necked flask (or in a conical flask with a cotton stoppered short funnel at its mouth). Heat at 130—135° in an oil bath (in its absence sand bath or on an asbestos centred wire-gauze). The contents first melt, then effervescence occurs and after 10—20 minutes the mixture foams up to three times its original volume and turns almost solid. Remove the flame and let it cool. Disintegrate the solid in the flask with about 15-16 ml. of water. Filter at the pump, wash with a little water and dry at 100°C. The substance melts at 233°. The yield is about 17 g. Recrystallise from methylated spirit, if necessary.

Third method and probably the best method.

5 g. phthalic anhydride
2·1 g. Urea
10 ml. glacial acetic acid.

Place the three substances in amounts noted against each together with a few boiling chips in a 100 ml. round bottomed flask fitted with an air condenser. Heat the mixture under reflux for ninety minutes. Adjust heating by controlling the flame in such a manner as the ring of the condensate rises only a few centimetres in the condenser. Solid may crystallise out during the course of heating. Let the contents of the flask cool down to room temperature. Filter by delivering the contents by gentle tapping of the flask and suck as dry as possible. Deliver the solid back to the flask and stir well with 10 ml. of water. Filter again and dry on a steam bath to constant weight. Determine the yield and note the melting point.

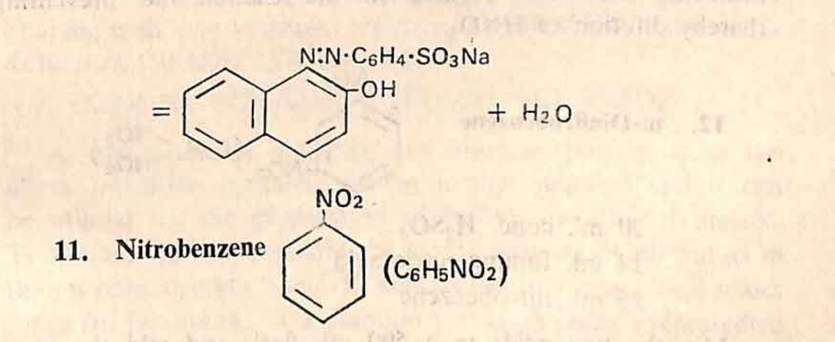
10. Naphthol organge



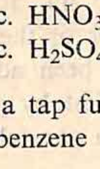
(sodium salt of sulphanilic-azo-β-naphthol)

3.5 gms. sulphanilic acid
3 gms. β-naphthol
4 ml. conc. hydrochloric acid diluted with 50 ml. water
1.5 gms. of sodium nitrite powder
25 gms. ice.
1.2 gms. caustic soda.

Mix in a beaker sulphanilic acid, hydrochloric acid and ice. When the temperature comes down to 0° add gradually the nitrite powder. Make in the meantime a solution of β-naphthol in alkali by dissolving 3 gms. of β-naphthol in 1·2 gms. of NaOH present in 20 ml. of water. Cool the solution. of β-naphthol by immersing the container in a bath of freezing mixture. When the temperature reaches 0°, add the diazotised solution a little at a time to this alkaline solution with constant stirring. Whilst keeping the mixture still in ice stir it for two hours. Filter the dark-red crystalline mass. Press on a porous earthenware and dry. The yield is about 7 gms.



11. Nitrobenzene



$(C_6H_5NO_2)$

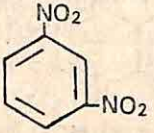
10 gms. benzene
12 ml. conc. HNO_3
12 ml. conc. H_2SO_4

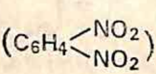
Add slowly from a tap funnel a well-cooled mixture of the above two acids to benzene taken in a 100 ml. flask. Shake the flask well after each addition. Note that the temperature must be kept below 50° by immersing the flask in cold water, if necessary. Nitrobenzene and acid divide into two layers; nitrobenzene floats as a brown oily layer on the acid mixture. When the addition is over, heat the mixture on water-bath for 20 minutes. Shake well the contents of the flask again. Cool and pour the contents of the flask into separating funnel and withdraw the lower acid layer. Wash the nitrobenzene free from acid by shaking first with water, then with a dilute solution of sodium carbonate and finally with water again—nitrobenzene being heavier sinks down and is removed each time from the bottom. Dehydrate the oil (nitrobenzene) by allowing it to stand over fused calcium chloride with occasional shaking. Decant the yellow liquid or filter from calcium chloride and distil with the help of a condenser tube only (without water circulation). At first a little benzene, if present, passes over. Collect the fraction coming between 204—207°. Neither distil to dryness nor allow the temperature to rise above 214°, as explosion may occur due to presence of higher nitro compounds, the formation of which is favoured if the temperature during nitration exceeds 50°. Yield is about 12 gms.

$$C_6H_6+HONO_2=C_6H_5NO_2+H_2O.$$

Sulphuric acid serves the purpose of a dehydrating agent removing the water formed in the reaction and preventing thereby dilution of HNO_3.

12. m-Dinitrobenzene





$$\left(C_6H_4<^{NO_2}_{NO_2}\right)$$

20 ml. conc. H_2SO_4
24 ml. fuming nitric acid
25 ml. nitrobenzene

Mix the two acids in a 500 ml. flask and add the nitrobenzene in portions of about 5 ml. at a time. Evolution of heat takes place and the colour of the mass deepens. When the whole of nitrobenzene has been added, heat the flask on water-bath for a short time. Test by pouring a few drops of the liquid from the flask into a test-tube containing water for completion of the reaction. Separation of a hard pale yellow cake of dinitrobenzene indicates the completion of the reaction. If, on the other hand, a semi-solid mass separates out, continue heating. Pour, while warm, the contents of the flask into a large quantity of water. Filter at the pump, wash the residue with water, recrystallise from spirit, dry and determine the melting point. Yield is about theoretical. Melting point of the substance is 90°. The reaction that takes place in this process is represented by the following equation:

$$C_6H_5NO_2+HNO_3=C_6H_4(NO_2)_2+H_2O.$$

13. Anisole (Methyl phenate, Phenyl methyl ether)

$C_6H_5\text{-}O\text{-}CH_3$

18.8 gms. phenol
24 ml. dimethyl sulphate
10 gms. caustic soda dissolved in 70 ml. water.

In a 250 ml. round flask dissolve phenol in caustic soda soultion. Add to it dimethyl sulphate in portions of 5 ml. at a time with vigorous shaking. Temperature rises and as it comes down within a few minutes, add again dimethyl sulphate as before taking care that the tempeature does not exceed 60°. When all the dimethyl sulphate has thus been added and the temperature begins to fall, heat the flask on water-bath for 10 minutes. Separate the upper oily layer of anisole, wash it by shaking with a little water, dry over calcium chloride and distil. It boils at 150-152°. Yield is 17 gms.

$$C_6H_5ONa+(CH_3)_2SO_4=C_6H_5OCH_3+CH_3NaSO_4$$

As the equation indicates, the aqueous portion from the above operation contains sodium methyl sulphate and it can be utilised for the preparation of further quantity of anisole. To the aqueous portion add the same quantity of phenol as in the previous operation and 10 gms. of caustic soda. Boil under reflux for five hours. The reaction that takes place is represented by the following equation.

$$C_6H_5ONa+CH_3NaSO_4=C_6H_5OCH_3+Na_2SO_4$$

SAMPLE QUESTIONS FOR VIVA VOCE

1. Inorganic Qualitative Analysis

(*A*) *Preliminary and some Special Tests*

Q. 1. Name a compound, which is red in colour.
Ans. Mercuric iodide (HgI_2)

Q. 2. Name a compound, which is brown in colour.
Ans. Ferric oxide (Fe_2O_3)

Q. 3. Name a compound, which is yellow in colour.
Ans. Cadmium Sulphide (CdS)

Q. 4. Name a compound which is black in colour.
Ans. Lead sulphide (PbS).

Q. 5. Name a green compound.
Ans. Chromic oxide, Cr_2O_3.

Q. 6. Name an orange red compound.
Ans. Antimony sulphide, Sb_2S_3.

Q. 7. Give the formula of each of the following substances:
(*i*) Silver chromate, (*ii*) ferric phosphate, (*iii*) calcium phosphate, (*iv*) silver arsenate, (*v*) copper (ic) arsenite, (*vi*) potassium arsenite, (*vii*) arsenic acid, (*viii*) phosphoric acid, (*ix*) mercurous iodide, (*x*) metaboric acid.

Ans. (*i*) Ag_2CrO_4, (*ii*) $FePO_4$, (*iii*) $Ca_3(PO_4)_2$ (*iv*) Ag_3AsO_4. (*v*) $Cu_3(AsO_3)_2$ (*vi*) K_3AsO_3, (*vii*) H_3AsO_4, (*viii*) H_3PO_4, (*ix*) Hg_2I_2, (*x*) HBO_2.

Q. 8. (*a*) State the colour exhibited by each of the following: (*i*) Dichromate, (*ii*) Chromate, (*iii*) Hydrated cupric salts, (*iv*) Co_3O_4, (*v*) CoS, (*vi*) $Cr(OH)_3$, (*vii*) Hg_2Cl_2, (*viii*) As_2S_3, (*ix*) Ferric hydroxide, (*x*) $SrCO_3$, (*xi*) $Mg(NH_4)PO_4$, (*xii*) $Pb(NO_3)_2$.

Ans. (*i*) Orange red, (*ii*) yellow, (*iii*) blue, (*iv*) black, (*v*) black, (*vi*) dirty green, (*vii*) white, (*viii*) yellow, (*ix*) brown, (*x*) white, (*xi*) white, (*xii*) colourless.

Q. 8. (*b*) Name the burner that you generally use in the laboratory?

Ans. Bunsen burner.

Q. 9. Why on heating in a test tube

(*i*) blue copper sulphate becomes white?

(*ii*) colours $Pb(NO_3)_2$ changes into a yellow substance?

(*iii*) red cuprous oxide changes to a black mass?

(*iv*) red mercuric oxide forms a shining mirror?

Ans. (*i*) Loss of water of crystallisation occurs, (*ii*) Lead nitrate decomposes into oxide of the metal. (*iii*) Cuprous oxide undergoes oxidation to cupric oxide. (*iv*) Mercuric oxide decomposes into metallic mercury, which is deposited on the cool er walls of the test tube.

Q. 10. What should you expect to observe when each of the following substances is heated in a test tube on being mixed with sodium carbonate:

(*i*) ammonium compounds, (*ii*) arsenic compounds?

Ans. (*i*) Pungent smell of ammonia, (*ii*) Garlic odour and formation of a shining black mirror in the cooler part of test tube.

Q. 11. Describe a preliminary test by which you can differentiate among the following

(*i*) Ammonium compounds, (*ii*) Mercury compounds and (*iii*) Arsenic compounds.

Ans. Heating of a mixture of the substance with four times its volume of anhydrous sodium carbonate. [See Page 8, expt. 1(a)]

Q. 12. How will you differentiate between the sublimates:

(*i*) Obtained by heating a mixture of mercury compound and sodium carbonate, (*ii*) Obtained by heating a mixture of arsenic compound and sodium carbonate?

(Both expts. are carried out in a test tube)

Ans. (*i*) Sublimate coalesces into globules of mercury on being rubbed with a moistened glass rod, (*ii*) Sublimate does not give any globlue on rubbing with a glass rod.

Q. 13. Name the compounds that may form metallic bead on heating in oxidising flame on charcoal block.

Ans. Compounds of silver, lead, bismuth and antiomny.

Q. 14. Describe a simple device of differentiating metallic bead of lead from those of silver, bismuth and antimony.

Ans. Lead bead marks paper while others fail to do so.

Q. 15. Is it necessary to carry out 'Cobalt nitrate test' as a method of routine analysis?

Ans. No.

Q. 16. How and when the cobalt nitrate test is carried out?

Ans. See Page 12, expt. 2(a) and the connected note (i.e. N.B.) given above it.

Q. 17. Should you use an excess of cobalt nitrate in the expt. named cobalt nitrate test?...If so, why so, if not, why not?

Ans. See the note described at the bottom of page 12.

Q. 18. Describe with a specific example the reactions that occur in cobalt nitrate test.

Ans. Cobalt nitrate undergoes decomposition by heat into CoO and this reacts with certain oxides with subsequent development of characteristic colour.

$$2Co(NO_3)_2 \longrightarrow 2CoO + 2N_2O_4 + O_2$$

$$CoO + Al_2O_3 \longrightarrow CoAl_2O_4 \text{ (blue)}$$

With excess of $Co(NO_3)_2$ the oxide CoO is formed in excess. The excess of the oxide CoO, under the experimental condition gets converted into cobaltic oxide Co_3O_4, which is black in colour. Hence this black colour will mask the distinctive colour, if excess of the reagent be used.

Q. 19. Name the colour obtained with the following substances in cobalt nitrate test: (*i*) Aluminium compounds, (*ii*) Zinc compounds.

State the formulae of the coloured substances giving the necessary equations for the reactions that lead to the formation of the coloured substances.

Ans. (*i*) Blue known as Thenard's blue.

(*ii*) Green known as Rinmann's green.

Thenard's blue $\longrightarrow CoAl_2O_4$

Rinmann's green $\longrightarrow CoZnO_2$

Equations of the reactions:

$$CoO + Al_2O_3 \longrightarrow CoAl_2O_4$$

$$CoO + ZnO \longrightarrow CoZnO_2$$

[The oxides of metal are first formed by decomposition of compounds of the metals on heating: e.g.; $ZnCO_3 = ZnO + CO_2$]

Q. 20. What colour should you expect to observe with magnesium compound in cobalt nitrate test? Give probable composition of the coloured mass.

Ans. Pink colour; probable composition of the coloured substance is MgO, CoO.

Q. 21. Give the formula of borax.

Ans. $Na_2B_4O_710H_2O$.

Q. 22. What happens when borax is heated?

Ans. Borax swells up, loses its water of crystallisation and finally forms a transparent glass-like bead, which is a mixture of sodium metaborate and boric anhydride.

$$Na_2B_4O_710H_2O = Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3$$

Q. 23.(*a*) What causes bead to be coloured in borax bead test?

Ans. Coloured beads are generally due to the characteristic colours of metaborates.

Q. 23.(*b*) What is the formula of copper metaborate? Explain how it is formed in borax bead test.

Ans. $Cu(BO_2)_2$.

When the bead is heated with a copper salt, the salt is converted into oxide of the metal, which reacts with boric anhydride (see ans. to Q. 22) forming copper metaborate.

$$CuSO_4 = CuO + SO_3, \quad CuO + B_2O_3 = Cu(BO_2)_2$$

Q. 24. What should you expect to observe in borax bead test with each of the following substances:

(*i*) Mn-compounds, (*ii*) Co-compounds?

Ans. (*i*) Colourless bead in reducing flame but amethyst violet in oxidising flame. (*ii*) Sapphire blue bead in both oxidising and reducing flame.

Q. 25. You are asked to carry out borax bead test with 'a little' of the sample.—why?

Ans. With too much of the substance the bead becomes saturated and may become opaque or so dark coloured that it may not be detected.

Q. 26. Say what inference or inferences you can draw from each of the following observations made by heating the substance mixed with sodium carbonate in reducing flame on charcoal block:

(*i*) Green residue left on charcoal,

(*ii*) Grey magnetic mass obtained,

(*iii*) Red flakes and spongy mass left on charcoal.

Ans. (*i*) Chromium compound, (*ii*) Compounds of Fe, Ni & Co. (*iii*) Copper compound.

Q. 27. Which acid is used in the flame test and why?

Ans. Chloride of metals being more volatile than other compounds impart characteristic colours to flame more readily and that is why HCl is used in the flame test.

Q. 28. Which is correct?

(*i*) Sodium obscures the flame colouration of potassium,

(*ii*) potassium obocures the flame colouration of sodium.

Ans. First one.

Q. 29. What is microcosmic salt?

Ans. Sodium ammonium phosphate $Na(NH_4)HPO_44H_2O$.

Q. 30. What is obtained as residue, when microcosmic salt is heated?

Ans. It is converted into sodium metaphosphate $NaPO_3$.

Q. 31. What causes the microcosmic bead to be coloured in O.F. ?

Ans. Sodium metaphosphate obtained on heating microcosmic salt dissolves many metallic oxides yielding orthophosphates. The orthophosphates often have characteristic colours.

Q. 32. Draw suitable inferences from each of the following observation:

(*i*) Blue coloured microcosmic bead is obtained,

(*ii*) Green (both hot and cold) coloured microcosmic bead is obtained.

(*iii*) Amethyst violet in O.F. but colourless microscomic bead in R.F.

Ans. (*i*) Cobalt compound, (*ii*) Chromium compound, (*iii*) Manganese compound.

Q. 33. 'With copper compounds both in Borax and Microcosmic bead tests the beads become ultimately red and opaque in R.F.'—Explain why.

Ans. The metaborate in contact with carbon of the reducing flame gets reduced first to cuprous metaborate and finally to metallic copper : $2Cu(BO_2)_2+C=Cu_2(BO_2)_2+B_2O_3+CO$

$$Cu_2(BO_2)_2+C=2Cu+B_2O_3+CO$$

In microcosmic bead test the orthophosphate formed in O.F. undergoes reduction to metallic copper in R.F.

$$CuNaPO_4+C=Cu+NaPO_3+CO$$

Colour of metallic copper is red and the formation of metallic copper thus makes the bead red and opaque.

Q. 34. Describe the fusion test for manganese and chromium.

Ans. See page 20, expt. 6(*i*)

Q. 35.(*a*) Mention the colour or colours obtained in the fusion test with manganese and chromium compounds.

Name with formulae the substances that cause the colour to appear.

Ans. Mn-compounds give green mass, while with chromium yellow mass is obtained.

The green colour is due to formation of sodium (with NaOH medium) manganate Na_2MnO_4. The formation of sodium chromate Na_2CrO_4 leads to the development of yellow colour.

Q. 35.(*b*) The yellow coloured mass obtained in fusion test for chromium, if allowed to be dissolved in water and then acidified undergoes a change in colour. What is the resulting colour and why does this change of colour occur at all?

Ans. Orange colour.

Conversion of chromate into dichromate;

$$2CrO_4''+2H^+\longrightarrow Cr_2O_7''+H_2O$$

Q. 36. How will you test for ammonium compound without the help of any liquid reagent?

State the equation for the reaction that occurs.

Ans. See expt. 6(*ii*), page 21.

$$(NH_4)_2SO_4+2NaOH=Na_2SO_4+2NH_3+2H_2O$$

Q. 37.(*a*) A sample was warmed with dil acid (HCl or H_2SO_4) in a test tube and a lead acetate paper was held at the mouth of the test tube. The paper turned black. What was the acid radical of the sample? Why does lead acetate paper turn black?

Ans. Sulphide.

Hydrogen sulphide evolved on warming with dil. acid. Lead acetate was converted into lead sulphide on coming in contact with hydrogen sulphide. Lead sulphide is black in colour.

$$MS+2HCl=MCl_2+H_2S\uparrow$$
$$PbAc_2+H_2S=PbS+2HAc$$

Q. 37.(*b*) Is there any gas which like CO_2 turns lime water milky?

Ans. Yes, Sulphur dioxide.

Q. 38. How do you differentiate among sulphide, sulphite and thiosulphate from their behaviour towards dil. acid?

Ans. A characteristic foul odour with sulphide due to evolution of hydrogen sulphide (*cf.* Q. 37).

Smell of burnt sulphur with both sulphite and thiosulphate due to evolution of sulphur dioxide. In addition to this thiosulphate gives a ppt. of sulphur, which distinguishes thiosulphate from sulphite.

$$MSO_3+H_2SO_4=MSO_4+H_2O+SO_2\uparrow$$
$$MS_2O_3+H_2SO_4=MSO_4+H_2O+SO_2\uparrow+S\downarrow$$

Q. 39. On treatment of a sulphite and/or thiosulphate with dilute acid a gas evolved which turned acidified dichromate green. What's this due to?

Ans. Sulphite or thiosulphate yields sulphur dioxide, which reduces dichromate to trivalent chromium compound.

$$K_2Cr_2O_7+H_2SO_4+3SO_2=\underset{\textit{green}}{Cr_2(SO_4)_3}+K_2SO_4+H_2O$$

Q. 40. How can you distinguish between a bromide & an iodide by a preliminary or so-called dry test?

Ans. The sample mixed with manganese dioxide is heated with conc. H_2SO_4 in a test tube:—

Evolution of brown vapours indicates bromide.

Evolution of violet vapours indicates iodide.

Q. 41. What should you expect to observe, when a nitrate is heated with conc. H_2SO_4.

How can you make this change a more prominent one?

Ans. Evolution of brown fumes.

The colour is intensified in presence of a few copper turnings. Hence the expt. is to be repeated with copper turnings.

Q. 42.(*a*) See the expt. stated in ans. to Q. 41 and name the coloured gas evolved in the expt. How does it form?

Ans. Nitrogen dioxide.

On heating a nitrate with H_2SO_4 nitric acid is liberated. The acid thus liberated undergoes thermal decomposition

$$4HNO_3=4NO_2+2H_2O+O_2.$$

In presence of copper turnings HNO_3 undergoes reduction easily to a mixture of nitrogen dioxide and nitric oxide. Any Nitric oxide first formed undergoes aerial oxidation to brown nitrogen dioxide.

$$2NO+O_2(\text{air}) = 2NO_2(\text{nitrogen dioxide})$$

Q. 42.(*b*) When a chloride is heated with dichromate and conc. H_2SO_4 a deep brownish red vapour evolves. What is this vapour?

Ans. Chromyl chloride CrO_2Cl_2 vapour.

Q. 43. What change should you expect to observe—

When the brownish red vapour obtained in the expt. described under Q. 42(*b*) is passed into caustic soda solution, then acidified with acetic acid and finally treated with lead acetate solution?

State the equations involved in the reactions.

Ans. The brownish red vapour dissolves in NaOH solution giving a yellow soln. of Na_2CrO_4. Finally $PbAc_2$ produces a yellow ppt. of lead chromate from this solution.

$$CrO_2Cl_2+4NaOH=Na_2CrO_4+2NaCl+2H_2O$$

$$Na_2CrO_4+PbAc_2=\underset{\textit{yellow}}{PbCrO_4}\downarrow+2NaAc.$$

Q. 44. Describe a test for fluoride.

Ans. See the expt. IV on page 29.

Q. 45. Note the expt. mentioned in ans. to Q. 44. Why does in the expt. the drop of water on a glass rod turn turbid? What is the formula of the substance that causes the water drop to be turbid?

Ans. The water drop turns turbid because of deposition of silicic acid. The formula of silicic acid is H_4SiO_4.

Q. 46. State with a suitable example the equations involved in the reactions for the expt. mentioned in ans. to Q. 44.

Ans. See the note (i.e., N.B.) given above the expt. V on page 30.

Q. 47. Describe perchromic acid test for chromate.

Ans. See the expt vi(a), page 31.

Q. 48. Note the expt. in Q. 47 and say what causes the blue colour to appear. Does this colour last long? If so why so? If not why not?

Ans. The blue colour is due to the formation of the so called perchromic (actually peroxide CrO_5) acid. It does not last long, as it decomposes yielding oxygen and a green solution of a chromic salt.

Equations for the reactions that occur:

$$4MCrO_4+4H_2SO_4 = 4MSO_4+2H_2Cr_2O_7+2H_2O$$
$$2H_2Cr_2O_7+8H_2O_2 = 4CrO_5+10H_2O$$
$$4CrO_5+6H_2SO_4 = 2Cr_2(SO_4)_3+6H_2O+7O_2$$

Q. 49. What reagents will you use for testing a phosphate?

Ans. Ammonium molybdate and nitric acid.

Q. 50. Name the compound that is precipitated in the test for phosphate with ammonium molybdate. What is the colour of the ppt.?

Ans. Ammonium phosphomolybdate is pptd. Colour of the ppt. is yellow.

Q. 51. State the necessary conditions for carrying out the molybdate test for a phosphate.

Ans. (*i*) The solution should not be heated to a temperature exceeding 40°C. (*ii*) Excess of reagents i.e., ammonium molybdate and conc. HNO_3 are to be used. (*iii*) Presence of a large amount of halide ions should be avoided.

Q. 52. Why is it that in ammonium molybdate test for a phosphate the solution should not be heated beyond 40°C?

Ans. Arsenates give similar reaction on boiling. Besides, silicates give yellow solution and white molybdic acid may separate out on boiling.

Q. 53. What is the necessity of using an excess of reagent in ammonium molybdate test for a phosphate? ,

Ans. For each PO_4^{3-} ions 12 MoO_3 units are necessary. The yellow precipitate of ammonium phosphomolybdate is soluble in alkalis, ammonia, alkali phosphates and excess of phosphoric acid. Hence, the use of excess of ammonium molybdate and nitric acid.

Q. 54. What additional reagent should you use in order to prevent interference from AsO_4^{3-} and SiO_3^{2-} while testing for a phosphate with ammonium molybdate?

Ans. 15-20% tartaric acid solution.

Q. 55. Describe alcohol flame test for boric acid.

Ans. See page 28, expt. III(a)

Q. 56. 'The mere production of a green-edged flame in alcohol flame test for borate is no proof of the presence of a borate.'—Why it is said so?

Ans. Free boric acid also produces the same green edged flame here. Hence, the presence of a borate should be reported, if boric acid is absent.

Q. 57. Is it essential to use sulphuric acid in alcohol flame test for boric acid?

Ans. No.

Q. 58. Is it necessary to use sulphuric acid in alcohol flame test for a borate?

Ans. Yes.

Q. 59. What causes the flame green in alcohol flame test for boric acid or borate?

Ans. Methyl or ethyl borate.

Q. 60. In alcohol flame test for boric acid or a borate which will you prefer and why: methyl alcohol, ethyl alcohol?

Ans. Free boric acid or boric acid liberated from a borate by the action of H_2SO_4 reacts with alcohol forming methyl or ethyl (according to the alcohol used) borate, which burns with a green edged flame.

$$Na_2B_4O_7 \xrightarrow{H_2SO_4} H_3BO_3$$

$$H_3BO_3 \xrightarrow{ROH} B(OR)_3 + H_2O$$

Methyl borate being more volatile than ethyl borate, the use of methyl alcohol is always preferred.

Q. 61. Describe 'silicon tetrafluoride test' for silicate.

Ans. See page 30, expt. V.

Q. 62. What is the cause of turbidity of water drop in 'Silicon tetrafluoride test' for silicate? State only the equaitons of the reactions involved in the change.

Ans. Deposition of white silicic acid on water drop makes the latter turbid.

For equations see page 30.

Q. 63. What is the formula of sodium nitroprusside? What colour does it give on reaction with sulphide ion? Give the formula of the coloured substance that results from the reaction.

Ans. $Na_2[Fe(CN)_5NO]$,

Violet colour, due to formation of $Na_4[Fe(CN)_5NOS]$

Q. 64. Give the equation for the reaction of sodium nitroprusside with an aqueous solution of sodium sulphide.

Does the nitroprusside give the reaction with free gas or hydrogen sulphide solution?

Ans. $Na_2S+Na_2[Fe(CN)_5NO]=Na_4[Fe(CN)_5NOS]$

Neither the hydrogen sulphide solution nor the free gas will give the reaction.

Q. 65. Mention a test to which all sulphur acids will respond.
Ans. See Page 32, expt. VII.

Q. 66. A little of barium sulphate mixed with anhydrous sodium carbonate is heated in a groove on characoal block in a reducing flame. A foul gas evolves, when a portion of the fused residue is treated with dil. HCl. What is the gas? State its smell and action (if there be any) on lead acetate paper.

Give equations showing the sequence of changes that leads to the formation of the gas from barium sulphate.

Ans. Hydrogen sulphide evolves. Its smell is similar to that of a rotten egg. It blackens lead acetate paper due to formation of lead sulphide.

$$BaSO_4+Na_2CO_3+4C \text{ (from charcoal)} =BaCO_3+Na_2S+4CO$$

$$Na_2S+2HCl=2NaCl+H_2S$$

(*B*) *Wet tests* :

Q. 1. Name the solvents that are to be tried for getting the substance in solution in order to detect the basic radicals.

Ans. (*i*) Water—cold and boiling, (*ii*) dil. HCl—cold & hot, (*iii*) conc. HCl—cold and hot, (*iv*) aqua regia or conc. HCl and a few particles of $KClO_3$.

Q. 2. In wet analysis for cations the solution of the substance obtained by boiling with water sometimes turns turbid on cooling.

What does this change indicate regarding the presence of cations?

Ans. Presence of Sn, Sb and Bi compounds.

Q. 3. Why should you use a small quantity of the substance for wet anaiysis of basic radicals? What is the general limit of the amount of substance that is to be taken for wet analysis of basic radicals?

Ans. With a large quantity of the substance, the ppt. will be so bulky that difficulties will be encountered in filtering, washing and finally disolving them.

Generally 0.5—1 gm. of the sample is to be taken for analysis.

Q. 4. What is a group reagent?

Ans. A group reagent separates a particular group of ions from ions of the groups (or group) that follow.

Q. 5. Does a group reagent separate metals of the particular group from those of the groups that precede it?

Ans. No.

Q. 6. What is the gr. I reagent?

Ans. Dil. HCl.

Q. 7. What are the metallic ions that comprise the gr. I?

Ans. Ag^+, Pb^{++}, Hg_2^{++}.

Q. 8. What is the special feature of the gr. I metallic ions?

Ans. Chlorides are insoluble in cold dil. HCl.

Q. 9. Give the formulae of the ppts. obtained on addition of dil. HCl to a solution containing metallic ions of silver group.

Ans. $AgCl$, $PbCl_2$, Hg_2Cl_2.

Q. 10. What is meant by the term 'solubility product'?

Ans. For sparingly soluble salts the product of the concentrations of the constituent ions raised to appropriate powers in a saturated solution of a given salt is a constant at constant temperature. This product is called the solubility product of the salt at the particular temperature.

Q. 11. Define 'solubility product' in terms of solution process.

Ans. The equilibrium constant for the solution process of a sparingly soluble salt is termed its solubility product at the temperature concerned.

Q. 12. When does the precipitation occur?

Ans. When the ionic concentration product of a sparingly soluble salt exceeds the solubility product of that salt, precipitation will occur.

Q. 13. Why is it that a slight excess of precipitant i.e., group reagent should always be added in order to precipitate out metals of a group for analysis?

Ans. To make the precipitation of the ions practically complete. Let us, for example, take the case of precipitation of AgCl in gr. I. In a saturated solution of silver chloride the equilibrium may be represented by: $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

$$\text{Hence, } K_s = C_{Ag^+} \times C_{Cl^-} \qquad \text{... (i)}$$

Where K_s is the solubility product of AgCl. Now group I reagent is dil. HCl, which dissociates into H^+ and Cl^- ions. Consequently when dil. HCl is added, C_{cl^-} in equation (*i*) increases. With this increased concentration product of the ionic concentration momentarily exceeds the solubility product of AgCl. In order to attain the solubility product value C_{Ag^+} must decrease and this can only occur by some AgCl going out of solution. In other words some Cl^- ions and Ag^+ ions combine to form solid AgCl, i.e., some silver chloride is thrown out of the solution as ppt. Since K_s is eqn. (i) is a constant, the greater the concentration of Cl^- ions the smaller is the concentration of Ag^+ ions in solution. Hence is the use of a slight excess of precipitant.

Q. 13(*a*) Should an excessive amount of the precipitant be used in the reaction of precipitation? If so, why so, and if not why not?

Ans. Only a slight excess is used. Use of a large excess may cause partial dissolution of the ppt. through complex formation. Furthermore it may cause complications at subsequent stages of analysis. The ppt., for example, may pass into colloidal state causing a lot of troubles. Last but not the least, an unnecessary excess is wasteful.

Q. 13(*b*). Why is it usually asked to add the precipitant to the hot medium and often with shaking or stirring?

Ans. Hot medium helps coagulation of the ppt. Stirring or shaking helps the crystals grow in size.

Q. 14. Dil. HCl precipitates out metals of gr. I as chlorides but fails to do so with metallic ions of subsequent groups. Why?

Ans. Cl^- ion concentration is increased due to addition of hydrochloric acid. The chloride ion concentration thus becomes sufficient to exceed the solubility product of AgCl, $PbCl_2$ and Hg_2Cl_2 but not sufficient to exceed the solubility product of the chlorides of metals of subsequent groups. Thus $PbCl_2$, Hg_2Cl_2 and AgCl only are pptd. in gr. I.

Q. 15. Name the gas used for precipitating basic radicals in order to classify the latter into analytical groups.

Ans. Hydrogen sulphide.

Q. 16. Name the II gr. reagents and the metallic ions that constitute the group.

Ans. Group reagents: H_2S in presence of dil. HCl.

Metallic ions : Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}

As^{+++}, Sb^{+++}, Sn^{++++}, Sn^{++}

Q. 17. What is the special feature of II gr. metals?

Ans. Sulphides insoluble in dil. HCl.

Q. 18. What should be the acid concentration of the solution in order to have the best result with H_2S in II group? What is the reason behind it?

Ans. See page 41;—In order to have the best result (i.e., the 4th line from the top).........and tend to form a stable sol (i.e., 14th line from the top).

Q. 19. How will you adjust the hydrogen ion concentration of the solution to precipitate out second group metals by hydrogen sulphide.

Ans. The filtrate from gr. I. or HCl solution of the sample is made just alkaline with NH_4OH (tested with litmus) by dropwise addition of the latter neglecting any ppt. that may come down. Now 1 c.c. 6(N)HCl per 20 c.c. of the solution is added, heated to boiling and H_2S passed. The filtrate or the solution as the case may be is diluted to three times with water and H_2S passed again as before.

Q. 20. Name the basic radicals that form the group IIA.

Ans. Mercury (*ic*), lead, bismuth, copper and cadmium.

Q. 21. Name the basic radicals that comprise the group IIB. Is there any special name for gr. IIA or gr. IIB ? What are the names, if there be any ?

Ans. Arsenic, antimony and tin.

Yes, Gr. IIA is also known as copper group while Gr. IIB as arsenic group.

Q. 22. State a property that distinguishes gr. IIA from gr. IIB.

Ans. Sulphide of gr. IIA metals are insoluble in yellow ammonium sulphide while those of gr. IIB are soluble in it.

Q. 23(*a*). How will you separate sulphides of gr. IIA metals from those of gr. IIB.

Ans. The pptd. sulphides are treated with yellow ammonium sulphide. The mixture is warmed, while stirring with a glass rod, cooled and filtered. The filtrate contains gr. IIB cations and the residue left over contains gr. IIA. The filtrate on acidification gives a ppt. of higher sulphides.

Q. 23(*b*). Why is yellow ammonium sulphide used instead of ordinary colourless ammonium sulphide in separating IIA & IIB basic radicals?

Ans. Among the gr. IIB sulphides SnS is insoluble in ordinary ammonium sulphide. Yellow ammonium sulphide is a polysulphide and an oxidising agent. It dissolves SnS.

Q. 24. What is yellow ammonium sulphide? State with equations (one example only) the role played by it in dividing the group II cations into subgroups A & B.

Ans. Yellow ammonium sulphide is a polysulphide $[(NH_4)_2S+S]$ and also an oxidising agent.

Of the sulphides of gr. II metals only arsenic, antimony and tin undergo dissolution on treatment with yellow ammonium sulphide forming thio-salts. The solution thus obtained on acidification with dil. HCl gives a ppt. of higher sulphides and the excess of yellow ammonium sulphide is decomposed at the same time. These basic radicals form gr. IIB, while the metals, whose sulphides are insoluble in yellow ammonium sulphide form gr. IIA.

$$As_2S_3+3(NH_4)_2S+2S=\underset{\text{ammouium thioarsenate}}{2(NH_4)_3AsS_4}$$

On acidification of thio-salt;

$$2(NH_4)_3AsS_4+6HCl=As_2S_5\downarrow+6NH_4Cl+3H_2S$$

Q. 25. In a medium acidified with dil. HCl hydrogen sulphide precipitates out metals of gr. II, while the sulphides of metals of subsequent groups are not pptd. under similar condition. —Explain why.

Ans. See page 47, 2nd paragraph.

Q. 26. What type of substance interferes with the precipitation of gr. II metals as sulphides (by the passage of H_2S through acidified solution)?

Give a few names of such substances. Illustrate the mode of interference by a suitable example.

Ans. Oxidising agents.

Ferric salts, chromates, arsenates and nitrites.

See page 41; From 3rd. line of 2nd paragraph : H_2S is first oxidised by......$2FeCl_3+H_2S=2FeCl_2+2HCl+S$.

Q. 27. Describe a method for removal of each of the following so that they are prevented from interfering with the precipitation of sulphides of II gr. metals by H_2S:

Sulphites, nitrates and nitrites.

Ans. See items (*i*) (*ii*) & (*iii*) on page 41.

Q. 28. How are chromates, arsenates and ferric salts prevented from interfering with the precipitation of sulphides of gr. II metals by H_2S.

Ans. SO_2-water i.e., sulphurous acid are added to the solution till the latter distinctly smells of it. Excess of sulphur dioxide is then boiled off.

Q. 29. It may so happen sometimes that a white ppt. appears while reducing chromates, arsenates etc. by boiling the solution with sulphurous acid.

Why does it occur at all?

What do you propose to do with the ppt.?

Ans. The ppt. is due to conversion of compounds of Pb, Ba, Sr and Ca (present singly or in a mixture) into their sulphates.

The ppt. is washed with water and the flame test performed. With the indication thus obtained the ppt. is treated as insoluble substance.

Q. 30. How will you separate $PbCl_2$ from a mixture containing $PbCl_2$, AgCl and Hg_2Cl_2?

How will you confirm the presence of lead in it?

Ans. By boiling with much water and filtering hot. $PbCl_2$ passes into filtrate.

For the rest see P. 54, the 3rd. column from the left. (i.e., the extreme right column of the table).

Q. 31. How will you separate in order to analyse:

a mixture of AgCl and Hg_2Cl_2?

What is the colour of the residue left over? What is this colour due to?

Ans. By treatment with warm 6(M) NH_4OH; when AgCl goes into solution forming a complex salt.

The residue turns black because of the separation of finely divided mercury.

Q. 32. How will you test for silver in an ammoniacal solution of silver chloride? Give equations for the reaction.

Ans. See Page 54, middle column of table-3.

For equations: See page 55, the 8th and the 9th line from bottom.

Q. 33. The metallic sulphides obtained by passing H_2S through solution containing all the metals of gr. IIA are washed with water and boiled for 2-3 minutes with dil. HNO_3.

What will be left over as residue?

Ans. Mercury sulphide & free sulphur.

Q. 34. Why is it that the IIA group sulphides are washed with water prior to dil. HNO_3 treatment?

Ans. The sulphides of gr. IIA metals are pptd. from a medium acidified with dil. HCl. The ppt., therefore, remains admixed with a fair amount of hydrochloric acid. Hence, if this be directly treated with nitric acid, a part or whole of mercury sulphide will go into solution by the action of mixed acid. That is why the ppt. is washed with water to make it free from hydrochloric acid.

Q. 35. What is alkali stannite? Why does the ppt. turn black when a few drops of alkali stannite is added on to the ppt. of $Bi(OH)_3$? Give equations.

Ans. To a solution of stannous chloride dil. solution of caustic soda is added dropwise until the initial white ppt. of stannous hydroxide *just* dissolves. The resulting solution is alkali stannite and it reduces bismuth hydroxide to metallic bismuth and hence the change of colour.

$$2Bi(OH)_3+3Na_2SnO_2=2Bi+3Na_2SnO_3+3H_2O$$

Q. 36. Explain how mercury is tested for in the IIA group ppt. obtained by the action of hydrogen sulphide?

Ans. See the last paragraph of page 56; 1st. and second paragraphs of page 57.

Q. 37. In the analysis of IIA group ppt. the filtrate obtained from ammonium hydroxide treatment is found to be coloured blue. What does this indicate regarding the presence of basic radical?

How will you confirm the presence of this basic radical in the filtrate?

Ans. Presence of copper compound.

For the rest see Table 5, page 58, extreme right column at the bottom.

Q. 38. Why is it necessary to acidify the ammoniacal filtrate before performing the confirmatory test for copper with potassium ferrocyanide?

Ans. To decompose the complex $[Cu(NH_3)_4]^{++}$ into Cu^{++} ions. Besides, ferrocyanide is decomposed by alkali.

Q. 39. Give the formula of potassium ferrocyanide. What is the colour of the ppt. obtained in the confirmatory test for copper with potassium ferrocyanide? Give the formula of the ppt.

Ans. $K_4[Fe(CN)_6]$.

Reddish brown or chocolate colour.

$Cu_2[Fe(CN)_6]$

Q. 40. Does cadmium interfere with the ferrocyanide test for copper?

Ans. No.

Q. 41. How can you detect cadmium in presence of copper?

Ans. See the extreme right column of the table-5, P. 58-59.

Q. 42. Is it necessary to use KCN in order to detect cadmium with H_2S in absence of copper?

Ans. No.

Q. 43. In presence of excess of KCN hydrogen sulphide precipitates out cadmium but not copper though the solubility product of copper sulphide is much smaller.—Explain why.

Ans. See the last but one paragraph of page 60.

Q. 44.(*a*) What will you observe:

(*i*) The ppt. of $PbSO_4$ (obtained in gr. IIA analysis) is boiled with conc. ammonium acetate solution;

(*ii*) The residue of arsenic sulphide (gr. IIB analysis) is gently heated with powdered ammonium carbonate and a little water?

Ans. (*i*) Lead sulphate dissolves.

(*ii*) Arsenic sulphide dissolves.

Q. 44. (*b*) See the ans. to Q. 44(a). The solution (*i*) is acidified with dil. acetic acid and potassium chromate added. The solution (*ii*) is acidified with dil. HCl. State the noticeable changes and explain with equations the reactions occurring in the processes.

Ans. See the third paragraph of Page 57 and the last paragraph of page 62.

Q. 45. Name the basic radicals that comprise gr. IIIA. What is the group reagent here?

Ans. Fe^{+++}, Al^{+++}, Cr^{+++}

Group reagent: NH_4OH in presence of NH_4Cl.

Q. 46. The metals of gr. IIIA are pptd. as hydroxides. NH_4OH alone can do the job. Why is then NH_4Cl used in conjunction with NH_4OH?

Ans. See the second paragraph of page 48.

On the other hand in absence of NH_4Cl, with undiminished OH^- ion concentration IIIA, IIIB, IV metals & Mg are pptd. as hydroxides, since the solubility product of their hydroxides are exceeded.

Q. 47. Can we use NaOH as group IIIA-reagent? If so, why so and if not, why not?

Ans. No, it can't be used.

Solution of NaOH is a strong electrolyte, dissociation is almost complete in solution. OH^- ion concentration is sufficient enough not only to exceed the solubility product of hydroxides of gr. IIIA metals but also those of hydroxides of gr. IIIB, IV and V (Mg) metals. Hence, caustic soda precipitates out group IIIA along with IIIB, IV and Mg—all as hydroxides.

Q. 48. (*a*) Can $NaCl+NaOH$ be used instead of NH_4Cl+NH_4OH as gr. IIIA reagent? Advance reasons in support of your answer.

(*b*) Can you use here $(NH_4)_2SO_4$ instead of NH_4Cl? If so, why so? If not, why not?

Ans. (*a*) No.

Dissociation of NaOH in solution is almost complete. The common ion (Na^+ ion being common) effect is negligible. The value of OH^- ion concentration in consequence is sufficient not only to exceed the solubility product of the hydroxides of gr. IIIA metals but also the same for the hydroxides of Grs. IIIB, IV and V (Mg.) metals. Furthermore, the mixure of NH_4Cl & NH_4OH has buffer action

(*b*) No. Barium, strontium etc., if present will be pptd. here as sulphates.

Q. 49. Name the acids that interfere with the usual scheme of analysis for basic radicals form gr. III onwards.

Ans. Boric, hydrofluoric, silicic and phosphoric acids.

Q. 50. What are generally known as interfering acids? When and how do they interfere?

Ans. See the ans. to Q. 49 and the last paragraph of p. 43.

Q. 51. A method for removal of interfering acids involves evaporation of the filtrate from gr. II. to dryness and repeated evaportion of this residue with conc. HCl.

What are these acids and in what form are they removed?

Ans. Boric and hydrofluoric.

Boric acid volatilises in the steam and HF volatilises with HCl.

Q. 52. As what compound is phosphate removed in $FeCl_3$ method?

Ans. $FePO_4$.

Q. 53. What are the advantages of $FeCl_3$ method of removal of Phosphoric acid?

Ans. See page 51.

Q. 53. (*a*) See Q. 51 and state what additional steps are to be taken in order to remove silicic acid.

Ans. Silicates decomposable by hydrochloric acid are converted into an insoluble form of SiO_2, if repeated evaporation followed by baking is resorted to. The mass is extracted with dil. HCl and SiO_2 filtered off.

Q. 54. Why is it that in passing from gr. II to gr. III the filtrate from gr. II is boiled with a few drops of conc. HNO_3 or bromine water after boiling off H_2S?

Ans. See the item 5 on page 43.

Q. 54. (*a*) Which will you use in the removal of phospate and why?—

Freshly prepared neutral ferric chloride, an aged solution of ferric chloride.

Ans. The first one. Aged solution contains free HCl and consequently affects the pH of the medium and leads to incomplete precipitation.

Q. 54. (*b*) How will make the given $FeCl_3$ solution neutral for use in phosphate separation?

Ans. By adding a dil. solution of ammonia till a slight permanent ppt. is formed, which is finally filtered off.

Q. 55. How will you separate $Fe(OH)_3$ from hydroxides of aluminium and chromium present in the gr. IIIA ppt.?

Ans. By boiling the ppt. with water and sodium peroxide till effervescence ceases. $Fe(OH)_3$ remains in the residue.

Q. 56. See the previous question and answer, and say what change or changes you expect to observe in the process. Explain with equations the reactions taking place during the process.

Ans. See the second paragraph along with the equations on page 64.

Q. 57. To a little of ferric chloride solution if a few drops of potassium ferrocyanide be added, a coloured ppt. comes down. What is the colour and to what is this due?

Ans. Prussian blue.

See the 1st. paragraph of page 65.

Q. 58. Name the metallic ions that comprise gr. IIIB. What is the group reagent here and what is the distinctive feature of the group?

Ans. Zn^{++}, Mn^{++}, Ni^{++}, Co^{++}. H_2S in presence of NH_4OH and NH_4Cl.

Feature: Sulphides soluble in acid but get precipitated in alkaline condition.

Q. 59. Which are likely to be precipitated by H_2S in acid medium:

(*i*) Sulphides having higher solubility product, (*ii*) sulphides with low solubility product?

Ans. The second type.

Q. 60. (*a*) Whose solubility product values are higher:

(*i*) Sulphides of gr. II metals, (*ii*) Sulphides of gr. IIIB metals?

(*b*) Why is it that H_2S is passed in ammoniacal medium in order to precipitate out IIIB gr. metals as sulphides?

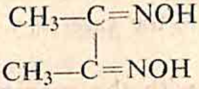
Ans. (*a*) Sulphides of gr. IIIB metals.

(*b*) See the last paragraph of page 47.

Q. 61. (*a*) What is the formula of dimethylglyoxime ?

(*b*) Name the metallic ion, whose presence is confirmed by this reagent.

Ans. (*a*)



$$\begin{array}{l} CH_3\text{—}C{=}NOH \\ \qquad\quad | \\ CH_3\text{—}C{=}NOH \end{array}$$

(*b*) Nickel (Ni^{2+}).

Q. 62. In a confirmatory test for manganese the pptd. hydroxide is boiled with HNO_3 and PbO_2 (or Pb_3O_4).

What change will you observe and why does it occur? Give equation showing this transformation.

Ans. Pink colour develops due to formation of MnO_4^- ion. For equation see the 5th. equation from top, page 68.

Q. 63. While precipitating out metals of gr. IV with the group reagents should you boil or warm the mixture after addition of ammonium carbonate?

Give your answer with plausible explanation.

Ans. See the 1st. paragraph (from the 6th. line from top) on page 45.

Q. 64. Name with formula the reagent used in detecting magnesium in the filtrate from gr. IV.

How you determine whether the ppt. obtained with the above reagent is a compound of aluminium or of magnesium?

Ans. Disodium hydrogen phosphate, Na_2HPO_4

For the rest see the note 2, on page 73.

Q. 65. Give the formula of sodium cobaltinitrite. What is the basic radical for whose identification it is used? Name with formula the compound formed making this identification possible. What is the colour of the compound?

Ans. $Na_3[Co(NO_2)_6]$.

Identifications of potassium.

Potassium-sodio-cobaltinitrite $K_2Na[Co(NO_2)_6]$. yellow.

Q. 66. What is the basic radical that interferes with the sodium cobaltinitrite test for potassium in gr. V? How will you carry out the test when this interfering radical is also present?

Ans. NH_4^+ ion interferes with this test. Besides, some ions belonging to gr. IIA and IIB interfere, but the question of the presence of these ions in gr. V does not arise at all.

For the rest: See the second paragraph of item 2 on page 74.

Q. 67. What is Nessler's reagent?

What colour or coloured ppt. as the case may be does the reagent produce with ammonia?

In order to carry out the test with this reagent it is often advised to heat the sample with alkali and allow the evolved gas to pass through it.—why?

Ans. See the note 5, pages 73-74.

Q. 68. Name a reagent used to detect Na^+ ion. Does the necessary reaction occur in acid medium? State with equation the changes that take place.

Ans. See the item 3 on page 74.

Q. 69. It may so happen sometimes that a ppt. comes down on addition of Na_2HPO_4 to the filtrate from group IV even when no magnesium is present. What's this due to?

Ans. See *N.B.* under the second paragraph, page 73.

Q. 70. To an acetic acid solution containing Sr^{++} and a small amount of Ca^{++} ammonia is added to make the solution alkaline. To the resulting alkaline mixture a saturated solution of ammonium sulphate is added, heated to boiling and then allowed to stand for five minutes.

State and explain what you expect to observe in the above process.

Ans. See the last paragraph of page 71.

Q. 70.(*a*) Why is it that magnesium carbonate, though insoluble in water is not precipitated in group IV?

Ans. In presence of NH_4Cl the high concentration of NH_4^+ ion lowers the CO_3^{--}ion concentration of the solution to such low a value as the solubility product of $MgCO_3$ is not attained.

Q. 70. (*b*) Can we use Na_2CO_3 as the group IV reagent? Advance reason in support of your statement.

Ans. No. The concentration of CO_3^{--} ion will be so high as the solubility product of $MgCO_3$ will be exceeded. Hence $MgCO_3$ also gets pptd. along with the carbonates of gr. IV. metals.

Q. 71. Describe the 'ring test' for nitrate.
What causes the brown coloured ring to be formed?
Ans. See expt. 4 page 78; and note 2 on page 79.

Q. 72. Find out the correct statement or statements:
In a mixture of nitrate and nitrite

(*i*) Nitrite inteferes with the test for a nitrate.
(*ii*) Nitrite can be identified even in presence of a nitrate.
(*iii*) Nitrate always interferes with the test for a nitrite.
(*iv*) Identification of a nitrate necessitates the prior removal of nitrite.

Ans. All save and except (*iii*) are correct

Q. 73. How will you decompose a nitrite for carrying out test for a nitrate? Give necessary equations.

Ans. See *N. B.* on pae 81.

Q. 74. In a test for halide (Br′ & I′) the prepared solution is treated with chlorine water in acid medium. Show by equation only the reaction involved in the change.

Ans. $2X^- + Cl_2 = 2Cl^- + X_2$, X = bromine, iodine.

Q. 75. How will you test for nitrate in presence of bromide and iodide? Give equations.

Ans. See the expt. (*a*) under mixture no. 7 on page 85.

Equations: (*i*) $NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O$; (*ii*) $3NaNO_3 + 8Al + 5NaOH + 2H_2O = 3NH_3 + 8NaAlO_2$.

Q. 76. See Q. 75 and say whether the nitrate can be identified or not by performing 'brown ring test' here.

Ans. No. Bromide and iodide must be absent. After the removal of bromide and iodide by nitrate free silver sulphate the test may however be applied.

Q. 77. See ans. to Q. 75 and say how by this test you can detect the presence of a nitrate in presence of ammonium ions.

Ans. See *N.B.* under the expt. 7 on page 85.

Q. 78. What characteristic change or changes should you expect to observe: When—

(*i*) To a portion of the neutral solution (prepared for identification of acid radical) containing *phosphate* and /or *iodide* an excess of $AgNO_3$ solution is added?

(*ii*) To a portion of the neutral solution (prepared for identification of acid radical) containing *thiocyanate* a dilute solution of $FeCl_3$ is added drop by drop?

(*iii*) A portion of the solution (prepared for identification of acid radical) containing *nitrate* is acidified with dil. H_2SO_4 and then a little of KI and starch solution are added?

(*iv*) A portion of the prepared solution containing *nitrite* and *iodide* is acidified with dil. H_2SO_4 and starch soluton added?

Should in any case no characteristic change occur what modification of the process you propose to do so as to cause the desired change to take place?

Ans. (*i*) A yellow ppt.; (*ii*) Blood red colouration; (*iii*) No characteristic change. If, however, the process is carried out by mixing another reactant i.e., a piece of zinc, a deep blue colour develops. (*iv*) A deep blue colour develops in solution.

Q. 79. Note the process (*iv*) described in Q. 78 and indicate in terms of equation the change or changes that occur.

Ans. $2NO_2' + 2I' + 4H^+ = 2NO + 2H_2O + I_2$

$\text{starch} + I_2 = \text{Starch iodide (blue)}$

Q. 80. How will you test for *arsenite* in a mixture containing arsenite, arsenate and phosphate?

Hints. After the separation of arsenate and phosphate (in ammoniacal medium) with magnesia mixture the filtrate is treated with H_2S as usual in acid medium, when a yellow ppt. of arsenious sulphide confirms arsenite.

Q. 81. See the Hints to Q. 80 and state the colour and formula of the ppt. obtained with magnesia mixture indicating the reactions involved by equations only.

Ans. White ppt. of $MgNH_4PO_46H_2O$ (magnesium ammonium phosphate) and $MgNH_4AsO_4\,6H_2O$ (magnesium ammonium arsenate).

$$HPO_4'' + MgCl_2 + NH_4OH = MgNH_4PO_4 \downarrow + 2Cl' + H_2O$$
$$HAsO_4'' + MgCl_2 + NH_4OH = MgNH_4AsO_4 \downarrow + 2Cl' + H_2O$$

Q. 82. What is magnesia mixture?

Ans. Solution containing $MgCl_2$, NH_4Cl and a little NH_4OH.

Q. 83. What change or changes will occur, when a ppt. containing a mixture of AgCl, AgBr & AgI is shaken with 4N $(NH_4)_2CO_3$, filtered and to the filtrate a few drops. of KBr solution added.

Ans. Of the three components AgCl only goes into solution from which KBr precipitates out yellowish white AgBr.

Q. 84. To the sodium carbonate extract containing S″, SO_3'', SO_4'' & S_2O_3'' an excess of $PbCO_3$ suspension is added and filtered. To the filtrate thus obtained an excess of $Sr(NO_3)_2$ solution is added and filtered. Name the acid radical (sulphur) present in the latter filtrate. How will you test for it?

Ans. S_2O_3'' remains in the filtrate.

For test : See the extreme right column of the table for mixture no. 4 on page 82.

Q. 85. Will you acidify the prepared solution before proceeding with the examination for sulphur acids in it?

Ans. No.

Q. 86. In a method for detection of bromide mixed up with an excess of iodide the latter is removed first and then the test for bromide is carried out in a medium made acidic with acetic acid by treatment with chlorine water as usual.

Describe a method for this removal of iodide explaining the reactions involved.

Ans. The prepared solution made acidic with acetic acid is treated with an excess of copper sulphate solution, when cuprous iodide is pptd. It is filtered. From the filtrate iodine is boiled off, the filtrate is made faintly alkaline with NaOH and filtered. With the resulting filtrate test for bromide is carried out after acidification with acetic acid.

Copper sulphate reacts with iodide, when iodine is liberated and a ppt. of cuprous iodide is obtained. $2CuSO_4+4I'=Cu_2I_2+I_2+2SO_4''$.

Cuprous iodide is removed by filtration, liberated iodine is boiled off and excess of copper ion is removed as $Cu(OH)_2$ by precipitation with NaOH.

(C) *Insoluble Residue or Sample.*

Q. 1. An insoluble residue (or sample) is green in colour. What preliminary tests you propose to perform with it for detecing the basic radical present?

Ans. Oxidising fusion (special) test.

Q. 2. For a white insoluble residue (or sample) what preliminary test or tests should especially be performed with a view to finding the basic radical (or radicals)?.

Ans. Cobalt nitrate test, Flame test and Fluorescent test.

Q. 3. Name the acid radicals that may remain associated with the insoluble residue or sample.

Ans. Halides, CrO_4'', S'', SO_4'' and SiO_3''.

Q. 4. Give only the names of preliminary tests that are to be carried out with the insoluble residue or sample with a view to finding the acidic radicals.

Ans. (*i*) Warming with conc. H_2SO_4, (*ii*) Warming with MnO_2 and conc. H_2SO_4, (*iii*) Silicon tetrafluoride test.

Q. 5. SnO_2 is insoluble but this on heating with sulphur and anhydrous sodium carbonate dissolves in water.

What's this change due to? What happens when this aqueous solution is acidified with dil. HCl?

Ans. See the 'reactions' described in second paragraph, page 93

Q. 6. Devise a simple method of separating out lead sulphate from a mixture containing $PbSO_4$, $BaSO_4$ and/or Silica.

Ans. Treatment with a conc. solution of ammonium acetate (made slightly acidic with HAc) at 70°C, when only lead sulphate goes into solution.

Q. 7. State the formula and colour of chrome iron stone.

Ans. $FeCr_2O_4$, dark-grey.

Q. 8. Describe fluorescent test for tin.

Ans. See page 90, expt. (ix).

Q. 9. What precautions should be taken while reporting for tin by fluorescent test?

Ans. See the *note* 2 on page 90.

Q. 10. If silicon dioxide and one or more of the ignited oxides of Fe, Al and Chromium be previously suspected in the insoluble residue or sample, which of the following reagents should be used for attacking the insoluble.

(*i*) sodium peroxide, (*ii*) acid potassium sulphate, (*iii*) caustic soda?

Ans. Acid potassium sulphate.

Q. 11. What visible change will occur, when fused lead chromate is fused with caustic soda and the resulting mass is treated with hot water?

Indicate the reaction by equation.

Ans. Fused lead chromate dissolves.

$$PbCrO_4+4NaOH=Na_2CrO_4+Na_2PbO_2+2H_2O$$

2. Qualitative Organic Analysis

Q. 1. What is the first step in class determination of an organic compound?

Ans. To find out the characteristic constituent elements present in the compound supplied.

Q. 2. What are the elements to be looked for?

Ans. Nitrogen, halogens and sulphur.

Q. 3. Is it worth while to test for carbon in the organic sample supplied? Justify your answer.

Ans. No.

Organic compounds are carbon compounds and hence carbon is to be tested for only when a compound is not definitely known to be organic.

Q. 4. What is a functional group?

Ans. The atom or a group of atoms that defines the structure of a particular class or family of organic compounds, and on which at the same time the properties of an organic compound primarily depend is called the functional group.

Q. 5. Whose method you generally follow in a laboratory for detecting the characteristic elements in an organic compound?

Ans. Lassaigne's method.

Q. 6. Name the reagent that is used in Lassaigne's method in order to convert the characteristic elements in an organic compound into easy detectable forms.

Ans. Sodium.

Q. 7. What colour of the flame in Beilstein's test indicates the presence of halogen?

Ans. Green.

Q. 8. 'Beilstein's test is more a negative test than a positive one'.—Discuss.

Ans. See the note 6, page 116.

Q. 9. What colour (or coloured ppt.) is given by nitrogenous organic compound when the filtrate from sodium fusion is treated with ferric chloride in the usual way? What's this colour (or ppt.) due to?

Ans. Prussian blue colour or ppt. depending on nitrogen content. Colour is due to formation of $Fe_4[Fe(CN)_6]_3$.

Q. 10. Read Q. 9 and explain with equations the changes that occur.

Ans. During fusion nitrogen of the organic compound combines with carbon and sodium to give sodium cyanide: $Na+C+N=NaCN$.

See also the second paragraph of p. 115 along with the equations.

Q. 11. Give the formula of sodium nitroprusside. What colour is given by the filtrate from sodium fusion of organic compound containing sulphur, when it (filtrate) is treated with nitroprusside solution?

Ans. sodium nitroprusside is $Na_2[Fe(CN)_5NO]$.
Violet colour.

Q. 12. In sodium nitroprusside test for sulphur in organic compound a violet colour develops. What's this colour due to? Show only by equation the reaction involved in the change.

Ans. Violet colour is due to formation of $Na_4[Fe(CN)_5NOS]$
Equation: $Na_2[Fe(CN)_5NO]+Na_2S=Na_4[Fe(CN)_5NOS]$

Q. 13. In ferric chloride test for nitrogen a blood red colour sometimes develops instead of prussian blue. What's this change due to? What plausible inference can be drawn from it?

Ans. The blood red colour is due to formation of thiocyanate, which indicates the presence of both nitrogen and sulphur.

Q. 14. How will you test for bromine and iodine in the organic sample ?

Ans. The expts. are carried out with the filtrate from sodium fusion of the sample.

For the rest: See the expts. (*iii*) & (*iv*) on pages 112-113.

Q. 15. State with equations the reactions that occur in the test common to halogens.

Ans. During fusion halogens, if present, combine with sodium giving sodium halides. The halide thus formed reacts with silver nitrate in presence of nitric acid giving the characteristic ppt. of silver halide.

$Na+X=NaX$, where X=a halogen atom

$NaX+AgNO_3=AgX+NaNO_3$

Q. 16. If either nitrogen or sulphur (or both) be present a modification of the usual test for halogens with $AgNO_3$ is essential. What is this modified procedure? What is the purpose of this modification?

Ans. The filtrate from sodium fusion is boiled with an *excess* dil. HNO_3 so as to reduce the volume to half. It is then cooled and treated with $AgNO_3$ solution.

For the rest: See the note 3, page 115.

Q. 17. If either nitrogen or sulphur (or both) be present boiling of the filtrate from sodium fusion with an excess of dil. HNO_3 is essential prior to treatment with $AgNO_3$ solution.

What are the troubles that might occur, if this is not done before addition of $AgNO_3$ solution?

Ans. If nitrogen is present a white ppt. of silver cyanide comes down, which may be mistaken for a halide even when no halogen is present. Besides, a black ppt. of Ag_2S appears, when sulphur is present and this black colour may mask the other colours.

Q. 18. Is it necessary to add a little caustic soda or caustic potash to the filtrate from sodium fusion in order to test with nitroprusside for sulphur in an organic compound?

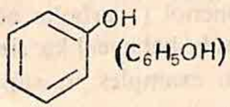
If so, why so? If not, why not?

Ans No, it is not necessary.

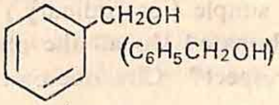
This test is always carried out in alkaline solution. But the excess of sodium left over and/or oxides that might be formed during the fusion react with water yielding caustic soda and thus make the solution alkaline.

Q. 19. What is the functional group of an alcohol? How does it differ from that of a phenol? Give examples.

Ans. The functional group of an alcohol is alcoholic hydroxyl. Both phenol and alcohol contain hydroxyl group—OH. In phenol the hydroxyl group remains **directly** attached to the aromatic ring. And this is known as phenolic hydroxyl.



phenol



benzyl alcohol

CH_3CH_2OH

ethyl alcohol

Q. 20. What colours are given by phenols, when treated with a drop or two of neutral $FeCl_3$ solution?

Ans. Any colour other than red and yellow.

Q. 21. Why is it necessary in a test for phenol to observe the effect of ferric chloride solution immediately after adding it?

Ans. The colour exhibited by some phenols is very much transitory in nature.

Q. 22. Why the red and yellow colour in ferric chloride test for phenol are neglected?

Ans. Reddish colouration or a ppt. is given by some carboxylic acids and yellow colouration is due to $FeCl_3$ itself.

Q. 23. (*a*) What is 'Back dye test'?

(*b*) Do all phenols respond to this test?

Ans. (*a*) See the item A(*i*), page 126.

(*b*) phenols with ortho- & para-positions blocked do not respond to this test.

Q. 24. (*a*) Name a class of compounds for which the following tests may be tried:

(*i*) Phthalein test, (*ii*) Liebermann's reaction.

(*b*) Does this class of compounds possess any characteristic smell?

Ans. (*a*) Phenols. (*b*) They usually possess a characteristic odour known as phenolic odour.

Q. 25. Which is usually more acidic?—

(*i*) phenols, (*ii*) carboxylic acid.

Ans. Carboxylic acid.

Q. 26. Describe a simple test for carboxylic group?

Ans. See expt. (*g*), page 118.

Q. 27. Name a reagent, which is usually used in detecting a carboxyl (—COOH) group.

Ans. Sodium bicarbonate.

Q. 28. What property of carboxyl group is utilised in bicarbonate test?

Ans. Acidic property.

Q. 29. Does simple (or ordinary) phenol (carbolic acid) react with bicarbonate? Do all the phenols behave like simple phenol is this respect? Cite one or two examples in support of your answer.

Ans. Ordinary phenol does not react with bicarbonate. Though phenols in general do not usually react with bicarbonate, certain types of phenols are there with which perceptible reactions occur. Chlorophenols, nitrophenols, for examples, give sufficiently strong acid reaction to produce effervescence with $NaHCO_3$.

Q. 30. Which is used for detecting a carboxyl group and why? —Na_2CO_3, $NaHCO_3$.

Ans. $NaHCO_3$ (and not Na_2CO_3) is used for detecting carboxyl group. Because: Na_2CO_3 reacts with both carboxylic acids and phenols; bicarbonate on the other hand does not usually react with phenols but produces effervescence with carboxylic acids. Secondly for a given amount of acid larger amount of CO_2 is evolved with bicarbonate.

Q. 31. Sodium carbonate though a stronger base than sodium bicarbonate is not used for detecting a carboxyl group.—why?

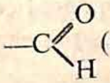
Ans. Because of stronger basicity it reacts with as weak an acid as phenol.

For the rest : See the ans. to Q. 30.

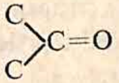
Q. 32 In a broad sense both aldehyde and ketone contain a common functional group. What is this group? Show by writing formulae the difference between aldehydic and ketonic functional groups.

Ans. Carbonyl group $>C=O$.

In an aldehyde at least one of the remaining valencies of carbonyl carbon is satisfied by a hydrogen atom, where as in a ketone both the valencies are satisfied either by alkyl or by aryl groups (or one by alkyl and another by aryl group). Hence the specific functional groups of aldehydes and ketones are:



(aldehyde),



(ketone)

Q 33. What is the reagent generally used in detecting a carbonyl group?

Ans. 2 : 4-dinitrophenylhydrazine.

Q. 34. Why is 2:4 dinitrophenylhydrazine, a derivative of phenylhydrazine used instead of phenylhydrazine itself in detecting a carbonyl group?

Ans. Because of comparatively ready crystallisation of the compounds formed with 2:4-dinitrophenylhydrazine.

Q. 35. What distinctive property is utilised in differentiating between an aldehyde and a ketone? Name two such reagents, which are generally used for the purpose.

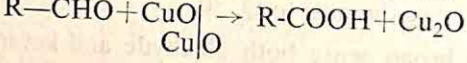
Ans. Aldehydes possess reducing property while ketones are usually devoid of it, they are resistant to oxidation. This difference in property is utilised in differentiating between the two.

Reagents : Fehling's solution, Tollen's reagent.

Q. 36. What is Fehling's solution? For what purpose it is used in qualitative organic analysis? State the visible change that occurs and indicate it by approximate equation.

Ans. It is a mixture of two solutions: Fehling's no 1 & no. 2. The first one contains aqueous solution of copper sulphate containing a few drops of H_2SO_4. The second one is an alkaline (NaOH) solution of sodium potassium tartrate.

It is used for differentiating between an aldehyde and a Ketone. A red ppt. of cuprous oxide appears.



$$\text{R—CHO} + \begin{array}{l|} \text{CuO} \\ \text{Cu}\end{array}\!\!\begin{array}{l}\\ \text{O}\end{array} \rightarrow \text{R-COOH} + Cu_2O$$

Q. 37. Is there any condition for mixing Fehling's no. 1 with Fehling's no. 2? If so, state these conditions.

Ans. Yes, They are to be mixed in *equal* volumes and *just* before use.

Q. 38. What is Tollen's reagent? How it is prepared?

Ans. Ammoniacal silver nitrate.

For preparation. See page 120, expt. (ii)

Q. 39. What is Schiff's reagent? What should you expect to observe when an aldehyde is allowed to react with this?

Ans. Schiff's reagent is magenta solution rendered colourless by sulphur dioxide. Aldehyde generally restores the charactistic magenta colour.

Q. 40. Name three reagents that are usually used to distinguish an aldehyde from a ketone.

Ans. Schiff's reagent, Tollen's reagent & Fehling's solution.

Q. 41. (*a*) Write down the formulae of:

2 : 4-dinitrophenylhydrazine, semicarbazide.

(*b*) Show only by equations the reaction of each of the above reagents with carbonyl compounds.

Ans. See the notes 4 & 5 on page 127.

Q. 42. (*a*) Which reaction is given by both aliphatic and aromatic $—NH_2$ group?

—Carbylamine reaction, Diazo-reaction and coupling.

Ans. Carbylamine reaction.

Q. 42 (*b*) Which reaction is charcteristic of an aromatic—NH_2 group? —Carbylamine reaction, Diazo-reaction.

Ans. Diazo-reaction.

Q. 43. What is carbylamine reaction? What's this characteristic obnoxious odour due to? Show only by equation the changes taking place.

Ans. The action of ethanolic alkali and chloroform on —NH_2 group is called carbylamine reaction. The obnoxious odour is due to formation of isocyanide.

For equation : See the note 10, page 128.

Q. 44. Show with a specific example by equations only the reactions occurring in Diazo-reaction and coupling.

Ans. See the note 11, pages 128-129.

Q. 45. Name a test by which —NO_2 group can be detected even in presence of a —NH_2 group.

Ans. Mulliken and Barker.

Q. 46. In Mulliken-Barker test a black or grey ppt. appears. What's this ppt. due to? Explain how this substance is formed here.

Ans. The ppt. is due to formation of metallic silver.

For the rest : See the note 12, page 129

Q. 47. Give the formula of amido group. How will you test for an amido group?

Ans. Formula of amido group is —$CONH_2$. Amide on heating with caustic soda gives off ammonia, which is recognised by its characteristic pungent odour [see the observation of expt. (*d*), page 123].

Q. 48. How does an amide differ from ammonium salts in its behaviour towards alkali?

Ans. In case of an amide ammonia is evolved *only* on heating alone.

Q. 49. What will you observe?—

(*i*) When $NaHCO_3$ is sprinkled on an aqueous solution of aniline hydrochloride, (*ii*) An amide is simply mixed with NaOH solution, (*iii*) A pale coloured nitro compounds is heated with NaOH solution.

Ans. (*i*) Effervescence occurs, (*ii*) No change, (*iii*) Colour deepens.

Q. 50. How will you test for nitro group in absence of $-NH_2$ group?

Ans. See the expt. (h), page 125.

Q. 51. (*i*) What happens to a $-NO_2$ group, when a compound containing such a group is boiled with metallic tin and conc. HCl.?

(*ii*) What happens when a portion of the supernatant liquid from the above process is cooled and treated with a cold aqueous solution of sodium nitrite?

(*iii*) What should you expect to observe when a portion of the supernatant liquid from process is made alkaline with strong alcoholic KOH and then warmed with a few drops of chloroform?

Ans. (*i*) $-NO_2$ group is reduced to $-NH_2$ group. (*ii*) $-NH_2$ group gets converted into $-N_2Cl$ group, (*iii*) A characteristic obnoxious odour evolves.

Q. 52. Should you consider effervescence with $NaHCO_3$ as a sufficient proof for the presence of a $-COOH$ group?

If so why so? If not why not? In the latter case what additional test should be performed before reporting its presence?

Ans. No. *For reasons*: see the note 3, page 127.

'Esterification' test (cf. Page 126) should be performed.

Q. 53. What type of substances produce colouration with $FeCl_3$ in ferric hydroxamate test? Show by equation only the formation of such compounds.

Ans. Hydroxamic acids. *For equation*: See the note 6, page 127.

3. Quantitative analysis

Q. 1. What is meant by normality of a solution?

Ans. Normality is the number of gm. equivalents of a solute present in one litre of its solution.

Q. 2. Calculate the equivalent weight of oxalic acid.

Ans. Oxalic acid is $(COOH)_2\text{-}2H_2O$. Hence mol. wt=126.

A dibasic acid, Eq. wt.$=\frac{1}{2}$ Mol wt. $\therefore$ Eq. wt. $=\frac{126}{2}=63.$

Q. 3. How much oxalic acid is to be weighed out in order to prepare 250 ml. of 0·1(N) solution of it?

Ans. See the 1st. paragraph under the item '*Standard soln. of oxalic acid*', page 215.

Q. 4. Fill up the blanks:

(*a*) 1 ml. (N) HCl $\equiv$ —ml. (N) NaOH
$\equiv$ —ml. (N) H_2SO_4
$\equiv$ —ml. (N) Na_2CO_3

(*b*) 1 ml. (N) HCl $\equiv$ —gm. NaOH
$\equiv$ —gm. Na_2CO_3
$\equiv$ —gm. $NaHCO_3$.

(*c*) 5 ml. —NaOH $\equiv$ 5ml. 0.1(N) $H_2SO_4 \equiv$ —ml.(N) H_2SO_4.

Ans. (*a*) 1, 1, 1; (*b*) 0·04; 0·053, 0·084; (*c*) 0·1(N), 0·5.

Q. 5. Which is invariant:
Eq. wt., Mol. wt.?

Ans. Mol. wt.

Q. 6. (*a*) Calculate the equivalent weight of $KMnO_4$ for oxidation-reduction reaction in (*i*) acid medium, (*ii*) neutral medium, (*iii*) alkaline medium.

Ans. (*i*) Partial ionic equation for reduction of $KMnO_4$ in acid medium : $MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$

$\therefore$ Eq. wt. $= \frac{1}{5}$ $KMnO_4 = 158/5 = 31{\cdot}6$

(*ii*) While in neutral medium the ionic equation is
$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^-$

$\therefore$ Eq. wt. $= \frac{1}{3}$ Mol. wt. $= 158/3 = 52.66$

(*iii*) In alkaline medium,
$MnO_4^- + e = MnO_4^{--}$
Eq. wt $=$ mol. wt.

Q. 6. (*b*) What is an indicator? Name an acid-base indicator stating the colour it exhibits in acid and alkaline medium.

Ans. An indicator is a chemical substance, which can indicate the termination of a chemical reaction. Methyl orange is an acid-base indicator, it is pink in acid and yellow in alkali.

Q. 7. Calculate the equivalent wt. of $K_2Cr_2O_7$ as an oxidising agent.

Ans. Partial ionic equation for reduction of dichromate:

$Cr_2O_7'' + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$

Hence, equivalent weight $= 1/6$ Mol. wt. $= \frac{294{\cdot}21}{6} = 49{\cdot}035$.

Q. 8. Calculate the amount of sodium oxalate necessary in order to prepare 250 ml. of 0·1(N) solution of it.

Ans. See the 1st & 2nd paragraphs under the topic named 'preparation of N/10 sodium oxalate solution', page 229.

Q. 9. (*a*) Give the formulae of:

(*i*) Potassium dichromate, (*ii*) Potassium permanganate & (*iii*) Mohr's salt.

(*b*) Calculate the mol. wt. of Mohr's salt and indicate its difference, if there be any, with its eq. wt.

Ans. (*a*) (*i*) $K_2Cr_2O_7$, (*ii*) $KMnO_4$.
(*iii*) $FeSO_4\ (NH_4)_2SO_4.6H_2O$.

(*b*) Mol. wt$=56+32+64+18\times2+32+64+108=392$. Since one ferrous ion per molecule of the salt is oxidised to ferric state by loss of one electron, there is no difference between the two : $Fe^{++}-e=Fe^{+++}$.

Q. 10. Pick out the substances that may be used as primary standard:

(*i*) Caustic soda, (*ii*) $KMnO_4$, (*iii*) $K_2Cr_2O_7$, (*iv*) H_2SO_4, (*v*) Sodium oxalate.

Ans. $K_2Cr_2O_7$, Sodium oxalate.

Q. 11. Give the equation for the oxidation of oxalic acid by acid permanganate.

Ans. See the clause (*iii*) under the item *N.B.* on page 232.

Q. 12. What is Zimmermann-Reinhardt solution?

Ans. Maganous sulphate solution containing sulphuric and phosphoric acids.

Q. 13. (*a*) Show only by equation the reduction of ferric chloride to ferrous chloride.

(*b*) What should be the acid concentration of the medium so as to have the above conversion a quantitative one?

Ans. See the '*principle*' described on page 234.

Q. 14. How would you know that in an experiment for estimation of iron the stannous chloride added is just sufficient to reduce the entire amount of ferric ion to ferrous ion?

Ans. Appearance of a silky white ppt. on addition of mercuric chloride is indicative of this point.

Q. 15. Why should you use Reinhardt in the determination of iron of a given ferric iron solution with permanganate?

Ans. To prevent oxidation of Cl' ion to Cl_2 by MnO_4^-.

Q. 16. Read the Q. 15 and explain the function of phosphoric acid in the above experiment.

Ans. It removes ferric ion in the form of colourless complex $[Fe(HPO_4)]^+$ ion. As a result:

(*i*) redox potential of Fe^{+++}/Fe^{++} system is reduced and reducing power of Fe^{++} is increased thereby;

(*ii*) secondly the yellow coloured Fe^{+++} ions being removed the end point is rendered more clearly visible;

(*iii*) moreover the Mn(III)—Mn(II) potential is lowered largely by phosphoric acid.

Q. 17. Fill up the gaps:

(*i*) 1 ml. of (N) $KMnO_4$ soln. ≡—g. of Fe.

(*ii*) —g. of iron≡0.392 g. of Mohr's salt.

Ans. (*i*) 0·056, (*ii*) 0·056.

Q. 18. Why is it that the decolourisation of permanganate is slow in the beginning in the standardisation of permanganate against oxalic acid?

Ans. Oxidation of oxalic acid by $KMnO_4$ is catalysed by Mn^{+2} ions. Because of the lack of these ions the reaction is slow in the beginning.

Q. 19. Is it necessary to use Reinhardt in the estimation of iron of a given ferric iron solution by dichromate?

Ans. No.

Q. 20. See the answer to Q. 19 and put forward an explanation for the same.

Ans. The redox potential of both Cr_2O_7''/Cr^{+++} and $Cl_2/2Cl^-$ is one and the same. Dichromate does not oxidise Cl′ ions unless the medium is heated and is more than 2(N) with respect to hydrochloric acid.

Q. 21. (*a*) Which is the stronger as oxidising agent?

$K_2Cr_2O_7$ or $KMnO_4$ (in acid medium).

Ans. $KMnO_4$.

Q. 21. (*b*) In presence of chloride ions the ferrous iron can not be titrated as such with permanganate but can be titrated with dichromate. Why?

Ans. See ans to Q. 20. and add the following:

Hence, Cl′ ion is not oxidised by Cr_2O_7'' under the experimental conditions and ferrous ion solution can, therefor[illegible]on.

titrated as such with dichromate. But permanganate being much stronger an oxidising agent than dichromate oxidises chloride to chlorine. Fe^{2+} is oxidised to higher unstable oxidation states (IV & V), which probably oxidise Cl^- ions, and Fe, therefore, acts as a catalyst in the oxidation of Cl^- by MnO_4^-. Hence the solution can not be titrated as such with permanganate.

Q. 22. Describe in an outline form the principle underlying the method of determination of iron of a given ferric iron solution with $KMnO_4$ or $K_2Cr_2O_7$ solution.

Ans. See the *principle* on page 234. Replace '$KMnO_4$' by '$KMnO_4$ or $K_2Cr_2O_7$'.

Q. 23. Why is it that a brown turbidity sometimes appears during the course of titration with $KMnO_4$? (Agra '54, Raj '65)

Ans. Absence of sufficient mineral acid leads to formation of hydrated manganese oxide.

Q. 24. Balance by ion electron method the equation for the reaction involved in each of the following processes:

(*i*) Titration of ferrous iron by (acid) permanganate.

(*ii*) Titration of ferrous iron by (acid) dichromate.

Ans. (*i*) (*a*) Ferrous ion is oxidised to ferric ion:

$$Fe^{++} - e = Fe^{+++}$$

(*b*) Permanganate is reduced to Mn^{++} ion:

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$

Since electron lost=electron gained, eqn. (*a*) is mutiplied by 5

$$5Fe^{++} - 5e = 5Fe^{+++}$$

Adding this resultant to the equation (*b*) the following complete ionic equation is obtained:

$$*5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O$$

(*ii*) Dichromate, while oxidising ferrous to ferric is reduced to Cr^{+++}: $Cr_2O_7^{--} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$

Now eqn. (*i*) (*a*) is multiplied by 6 and added to this [i.e. eqn, (*ii*)]:

$$**Cr_2O_7^{--} + 6Fe^{++} + 14H^+ = 6Fe^{+++} + 2Cr^{+++} + 7H_2O$$

Q. 25. Read the equations in ans. to Q. 24 and calculate the amount of iron equivalent to:

(*a*) 1 ml. of (*N*) $KMnO_4$

(*b*) 1 ml. of (N) $K_2Cr_2O_7$

Ans. (*a*) From the * marked equation

$1MnO_4^- \equiv 5Fe^{++}$ or, 1/5 of $MnO_4^- \equiv 1Fe^{++} = 56$ gms.

$$\text{Eq. wt. of } KMnO_4 \text{ (acid medium)} = \frac{Mol.\ wt.}{5}$$

1000 ml. (N) $KMnO_4 \equiv 56$g. of iron

1 ml. ,, $\equiv 0.056$,,

(*b*) From ** marked equation

$1\ Cr_2O_7'' \equiv 6Fe^{++}$ or $\frac{1}{6}$ of $Cr_2O_7'' \equiv 1Fe^{++} = 56$ gms.

$$\text{Eq. wt. of } K_2Cr_2O_7 = \frac{mol.\ wt.}{6}$$

1000 ml. of (N) $K_2Cr_2O_7 \equiv 56$g. of iron.

1 ml. ,, $\equiv 0.056$,,

Q. 26. Calculate from the general concept of equivalence the amount of iron equivalent to:

(*i*) 1 ml. of 0·1(N) $KMnO_4$ (in the determination of iron by $KMnO_4$)

(*ii*) 1 ml. of 0.1(N) $K_2Cr_2O_7$ (in the determination of iron by $K_2Cr_2O_7$)

Ans. (*i*) 1 gm-equivalent of $KMnO_4 \equiv 1$ gm-equivalent of Fe^{++}

$\therefore$ 1000 ml. of (N) $KMnO_4 \equiv 1$ gm-atom of $Fe \equiv 56$ gms. of Fe [Since transfer of one electron takes place in the conversion of $Fe^{++} \longrightarrow Fe^{+++}$]

$\therefore$ 1 ml. of (N) $KMnO_4 = 0.056$ gm. of Fe

or, 1 ml. of 0.1(N) $KMnO_4 = 0.0056$ gm. of Fe

(*ii*) 1 gm.-equivalent of $K_2Cr_2O_7 \equiv 1$gm. equivalent of Fe

$\therefore$ 1000 ml. of (N) $K_2Cr_2O_7 \equiv 56$ gms. of Fe

or 1 ml. of 0.1(N) $K_2Cr_2O_7 \equiv 0.0056$ gm. of Fe.

Q. 27. In permanganometric estimation of calcium calculate with the help of general concept of equivalence what amount of calcium is equivalent to 1 ml. of 0·1(N) $KMnO_4$.

Ans.

1 gm-equivalent of $KMnO_4 \equiv 1$ gm-equivalent of oxalic acid $\equiv 1$ gm-equivalent of $CaC_2O_4 \equiv \frac{1}{2}$ gm-molecule of CaC_2O_4

$\equiv \frac{1}{2}$ gm-atom of Ca

$= 20$ gms. of Ca

$\therefore$ 1000 ml. (N) $KMnO_4 \equiv 20$ gms of Ca

1 ml. of 0·1(N)$KMnO_4 \equiv 0.002$g. of Ca.

Q. 28. Arrange the following in order of their increasing oxidising power: $K_2Cr_2O_7$, I_2, $KMnO_4$

Ans. $I_2 < K_2Cr_2O_7 < KMnO_4$, permanganate is the strongest.

Q. 29. What is the formula of sodium thiosulphate? Can it be used as a primary standard? If so, why so and if not, why not?

Ans. See the 1st paragraph of the topic named '*Preparation of standard solution of sodium thiosulphate*', page 241.

Q. 30. Write the equation for the reaction between thiosulphate and iodine and hence show the relationship between the mol. wt. and the equivalent wt. of thiosulphate.

Ans. See the 2nd. paragraph of the topic named 'preparation of standard solution of sodium thiosulphate'. page 241.

Q. 31. Write the partial ionic equation for oxidation of sodium thiosulphate to tetrathionate and hence calculate its eq. wt.

Ans. $2S_2O_3'' - 2e \rightarrow S_4O_6''$

Mol. wt. of $Na_2S_2O_3.5H_2O = 46+64+48+90 = 248$

Since two molecules lose two electrons, the equivalent wt. of thiosulphate is its mol. wt.

Q. 32. Calculate the amount of $K_2Cr_2O_7$ equivalent to 1 ml. of 0·1(N) thiosulphate in iodometric determination.

Ans. 1 gm-equivalent of thiosulphate

$\equiv$1 gm-equivalent of $K_2Cr_2O_7$

or 1000 ml.(N)$Na_2S_2O_3$ solution$\equiv$49g. of $K_2Cr_2O_7$

1 ml. 0.1(N) ,, $\equiv$0.0049 g. ,,

Q. 33. Establish the quantitative relationship involved in iodometric estimation of copper among the following:

Cu^{++}, I_2 and sodium thiosulphate.

Hence calculate what amount of copper is equivalent to 1 ml. of 0·1(N) thiosulphate.

Ans. The reaction between cupric salt and iodide:

$$2Cu^{++} + 4I' = Cu_2I_2 + I_2$$

Iodine thus liberated oxidises thiosulphate to tetrathionate:

$$2S_2O_3'' + I_2 = S_4O_6'' + 2I'$$

From the two above reactions we can write

$$2\ Cu^{++} \equiv I_2 \equiv 2S_2O_3''$$

or, $Cu^{++} \equiv \frac{1}{2}I_2 \equiv S_2O_3''$

or, 1000 ml. of(N) thiosulphate $\equiv$63·57 g. of copper

∴ 1 ml. of 0·1(N) ,, $\equiv$0.006357 ,,

Q. 34. Why is ammonium thiocyanate added *in the iodometric* estimation of copper with sodium thiosulphate?

Ans. See the item no. 4 on page 246.

Q. 35. Why in iodometric estimation the presence of an excess of iodide is a must?

Ans. To complete the reduction of whole amount of oxidant iodide must be in excess. Besides, the liberation of iodine from iodide by the oxidant is facilitated, and the volatility of iodine is decreased considerably through the formation of tri-iodide ion and liberated iodine can thus be retained in soln. So during subsequent titration with S_2O_3'' sharp end point can be obtained.

Q. 36. Why is iodometric titration conducted in the cold?

Ans. To minimise the loss of iodine through volatilisation. Titration should be conducted also in the cold because the sensitivity of starch as indicator decreases with the rise of temperature.

Q. 37. Which of the following vessels is used in iodometric estimation and why: Opern beaker, conical flask?

Ans. Conical flask; to prevent as far as practicable the loss of iodine through volatilisation.

Q. 38. What is the maximum pH at which iodometric titration, if necessary may be conducted? What happens if pH of the medium exceeds this value?

Ans. In no case the solution pH should exceed 9. At lower acidities i.e., above pH 9 iodine reacts with hydroxide ions in accordance with the equation:

$$I_2+2OH^- = I^-+IO^-+H_2O$$

With hypoiodite oxidation of thiosulphate partially to sulphate occurs : $S_2O_3''+4IO^-+2OH^-=2SO_4''+4I^-+H_2O$

The greater the OH^- ion concentration, the more thiosulphate is oxidised into sulphate. Because of this side reaction calculation of analyticl result becomes an impossible one.

Q. 39. How may the possible errors in iodometric estimation due to aerial oxidation of iodide be eliminated or reduced?

Ans. In neutral medium the extent of aerial oxidation of iodide is negligible and can be ignored. In acid medium the solution should not be left over for a period longer than necessary prior to titration of iodine. If and when prolonged standing is necessary, a little of pure $NaHCO_3$ is added to the acid solution.

A stream of carbon dioxide displaces air from inside, maintains an atmosphere of its own within the reaction vessel and this prevents the iodide from being oxidised by air.

Q. 40. When should you add starch indicator in titrating iodine with thiosulphate? Put forward a plausible explanation for your answer.

Ans. Starch should be added as close to the end point as possible, i.e., when the concentration of iodine is very small. If, on the other hand, starch be added much ahead of the end point, i.e., when the iodine concentration is high, some amount of iodine may remain adsorbed even when the requisite volume of thiosulphate has been added. This will evidently lead to high result.

Q. 41. Why does a solution of starch in water deteriorate rapidly on storage?

Ans. Starch solution is a very good nutrient medium for microorganisms and hence undergoes rapid deterioration.

Q. 42. (*a*) How would you know that a given starch solution has undergone deterioration?

Ans. To a drop of N/50 iodine solution contained in 50 ml. water 2 ml. starch solution is added.—Development of blue colour indicates that the solution is all right. If, on the other hand, the colour is not blue but brown or violet, the given starch solution is unsuitable as indicator, it has undergone deterioration.

Q. 42. (*b*) What is iodometry and what is iodimetry?

Ans. It is a branch of volumetric analysis and it deals with the use of iodine involving the interconversion of elemental iodine and iodide ions: $I_2 + 2e \leftrightharpoons 2I^-$. Iodometry covers titrations of iodine liberated in chemical reactions, while iodimetry is concerned with titrations with a standard solution of iodine.

$CuSO_4 + KI$ against S_2O_3''—Iodometry

Standard I_2 solution against S_2O_3''—Iodimetry.

Q. 43. How may the keeping quality of starch solution be improved?

Ans. Addition of a few milligrams of HgI_2 to starch-potassium iodide solution makes the solution more stable. Addition of 5 mg. of mercuric iodide, for example, to 100 ml. of 1 % solution will preserve it for several months.

Q. 44. What are the reasons for the instability of thiosulphate solution?

Ans. (*i*) Carbonic acid present in ordinary distilled water may react slowly with thiosulphate with the liberation of sulphur.

(*ii*) Some micro-organisms may cause decomposition of thiosulphate. Besides, exposure to light hastens the decomposition of thiosulphate.

Q. 45. Read the answer to Q. 44. State and explain the effect of each on the strength of thiosulphate solution.

Ans. Thiosulphate reacts slowly with dissolved carbonic acid as follows: $S_2O_3'' + H^+ = HSO_3^- + S \downarrow$

S_2O_3'' reacts with one atom of iodine, while HSO_3' with two atoms of iodine. The equivalent wt. of thiosulphate is its molecular weight while that of bisulphite is half of its molecular weight. One HSO_3' ion is produced from one S_2O_3''. Hence the strength (normality) of thiosulphate solution prepared in water containing carbon dioxide increases as the reaction proceeds.

For reasons outlined under item (*ii*) in ans. to Q. 44. the strength of thiosulphate solution tends to decrease.

Q. 46. What should you propose to do in order to avert the reaction of thiosulphate with carbonic acid?

Ans. Solution of thiosulphate is to be prepared in freshly boiled distilled water. Besides, addition of 0.1g. of Na_2CO_3 or borax per litre of the solution will prove beneficial.

Q. 47. (*a*) How may the bacterial action upon thiosulphate be prevented? (*b*) Why is thiosulphate solution stored in amber-coloured bottle?

Ans. (*a*) 3 drops of chloroform or 10 mg. of mercuric iodide per litre of the solution may be added to prevent the decomposition of thiosulphate by microorganism.

(*b*) To avoid the action of light, which hastens the decomposition of thiosulphate.

Q. 48. Explain the role played by sodium carbonate in improving the keeping quality of sodium thiosulphate solution.

Ans. Sodium carbonate provides CO_3^{--} ions, which combine wth H^+ ions of carbonic acid and thus prevents the latter from reacting with thiosulphate. Moreover, the activity of micro-organism is the least at pH 9-10; the presence of sodium carbonate in amounts, not exceeding 0·1gm/litre, is beneficial.

Q. 49. What are to be done in order to improve the keeping qualities of thiosulphate solution?

Ans. (*i*) Solution of thiosulphate is prepared in freshly boiled distilled water (i.e. water free from carbon dioxide as far as possible).

(*ii*) 0.1 g. sodium carbonate & 3 drops of chloroform or 10 mg. of mercuric iodide (per litre of the solution) are added.

(*iii*) The solution is finally stored in amber-coloured bottle and preferably in the dark.

Q. 50. What is the function of bifluoride in the estimation of copper in brass? Is it a must in the determination of copper in copper wire? If so, why so and if not, why not?

Ans. Iron in brass is present in the solution made as ferric ions, which are suppressed by bifluoride as complex $[FeF_6]^{3-}$. If this is not done, ferric ions under the condition of the expt. will oxidise iodide to iodine: $2Fe^{+++}+2I^- \rightarrow 2Fe^{++}+I_2$. Thus the expt. will be vitiated. Moreover, NH_4HF_2 maintains the correct pH for iodometric estimation of copper.

In case of copper wire the use of bifluoride is not essential, since no iron is present. Glacial acetic acid may be used instead of bifluoride.

Q. 51. What is the molecular formula of glucose? Name the functional group or groups present in glucose.

Ans. Molecular formula of glucose is $C_6H_{12}O_6$. Aldehydic group and alcoholic hydroxyl groups are present in glucose.

Q. 52. 'Estimation of glucose by Fehling involves oxidation-reduction'. What is the oxidant and what is the reductant here?
Ans. Glucose is the reductant and Fehling is the oxidant.

Q. 53. In the estimation of glucose by Fehling—

(*a*) reaction of what functional group of glucose is utilised?

(*b*) what is the active species in Fehling?

(*c*) state the ultimate fate of each species in the reaction.

Ans. (*a*) aldehyde group, (*b*) Cu^{++} ion, a small concentration of which is furnished by copper tartarate complex, (*c*) aldehyde group is converted into $—COO^-$ and the Cu^{++} is reduced to red Cu_2O.

Q. 54. What is formalin?

Ans. A solution of formaldehyde containing 40% formaldehyde, 8% methanol and 52% water is known as formalin.

Q. 55. In the determination of formaldehyde in formalin which of the following is believed to be the real oxidant, that oxidises formaldehyde to formic acid:

I_2, NaOH, OI′ ?

Ans. OI′

Q. 56. State and explain the part played by caustic soda in the expt. named 'estimation of formaldehyde'.

Ans. Under the experimental conditions iodine and caustic soda reacts with the formation of iodide and hypoiodite:

$$I_2 + 2NaOH = NaI + NaOI + H_2O$$

A part of hypoiodite is utilised in oxidising formaldehyde to formic acid: $CH_2O + OI' = HCOOH + I'$

Caustic soda being in excess converts the formic acid into sodium formate: $HCOOH + NaOH = HCOONa + H_2O$.

Q. 57. State with equation the reaction, that leads to the liberation of iodine in the expt. named 'estimation of formaldehyde'.

Ans. In acid medium hypoiodite oxidises iodide to iodine:

$$OI' + I' + 2H^+ \rightarrow I_2 + H_2O.$$

Q. 58. Read the answer to Q. 57 and point out the sources of this iodide.

Ans. Two sources are there: (*i*) reaction between iodine and alkali (see the first paragraph of the ans. to **Q.** 56). (*ii*) oxidation of formaldehyde to formic acid (see the second paragraph of the ans. to Q. 56).

Q. 59. What is the formula of potassium bromate?

Ans. $KBrO_3$

Q. 60. Calculate the equivalent weight of potassium bromate as an oxidising agent.

Ans. Potassium bromate reacts with potassium bromide in acid medium in accordance with the equation.

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

Equivalent weight of $KBrO_3$ here is, therefore, $\frac{1}{6}$th of Mol. wt.
Molecular weight of $KBrO_3 = 39.1 + 79.92 + 48 = 167.02$

$\therefore$ Eq. wt. ,, $= 167.02/6 = 27.8367$

Q. 61. What amount of $KBrO_3$ is to be weighed out in order to prepare a 250 ml. solution of 0·1(N) order?

Ans. Equivalent weight of $KBrO_3$ is 27.8367. (cf Q. 60) Hence, 250 ml. of a 0.1(N) solution should contain (2.7836/4)g. =0.6959g.

Q. 62. Deduce the quantitative relationship that exists among aniline, bromine, iodine and thiosulphate in the experiment named 'determination of aniline by bromination'.

Ans. See the "theory" on page 261.

Q. 63. What is the mol. wt. of aniline? How many gms. of aniline are equivalent to 1 ml. of 0.1(N) thiosulphate?

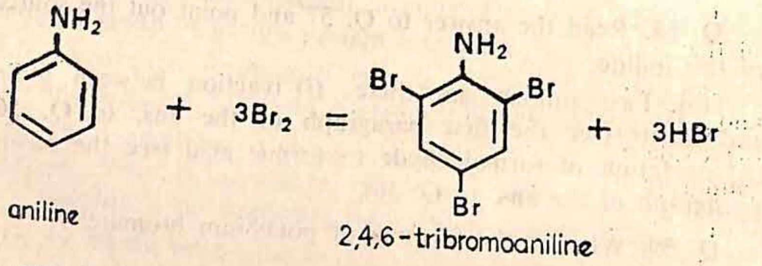
Ans. Mol. formula of aniline is $C_6H_5NH_2$ and hence its mol. wt. is 93.12. 1 ml. of 0.1(N) thiosulphate is equivalent to 0.00155g. of aniline [See the theory on page 261.]

Q. 64. How many molecules of thiosulphate are equivalent to one molecule of aniline?

Ans. $1C_6H_5NH_2 \equiv 6Na_2S_2O_3$. (*See the theory on page 261.*)

Q. 65. What property of aniline is utilised in determining it iodometrically?

Ans. The reaction between aniline and bromine is quantitative. Aniline on reaction with bromine gives a precipitate of 2, 4, 6-tribromoaniline.



This is the property, which is utilised in estimating aniline.

Q. 66. What is the functional group in aniline? Does the functional group get involved directly in the reactions concerning the estimation of aniline?

Ans. Primary amino (—NH_2) group.

The functional group does not take part directly in the reactions concerned.

Q. 67. What is the source of bromine, that is utilised for bromination of aniline in determining the latter? Give the necessary equation.

Ans. The reaction between bromate and bromide in an acid medium leads to the liberation of bromine, which in turn brominates aniline.

$$KBrO_3+5KBr+6HCl=3Br_2+6KCl+3H_2O$$

Q. 68. State with equation the reaction, that leads to the liberation of iodine in the experiment named 'determination of aniline'.

Ans. Bromine liberates iodine from potassium iodide:

$$Br_2+2KI = I_2+2KBr$$

4. Organic Preparations

Q. 1. What is iodoform? To what class of organic compound does it belong?

Ans. Tri-iodomethane CHI_3. A halogen derivative of hydrocarbon.

Q. 2. Name the organic substances from which iodoform is usually prepared in the laboratory. What is the name of the reaction involved in this preparation?

Ans. Ethyl alcohol or acetone
Haloform reaction.

Q. 3. Is the haloform reaction restricted to ethyl alcohol and acetone? Does methyl alcohol respond to this test?

Ans. No.
No.

Q. 4. What type of compounds exhibit haloform reaction?

Ans. Any compound containing —$COCH_3$ group linked to a carbon or hydrogen, or compounds which under the experimental conditions are oxidisable to a substance containing this group exhibit the reaction.

Q. 5. What is the formula of acetanilide? To what class of organic compound does it belong?

Ans. $C_6H_5NHCOCH_3$, anilide

Q. 6. What is an anilide? Name an anilide with which you are familiar.

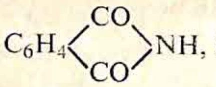
Ans. N-phenyl derivative of the amide of any acid is termed an anilide. Acetanilide $C_6H_5NHCOCH_3$ is a familiar anilide.

Q. 7. What is acylation? Illustrate with an example by giving equation only.

Ans. Introduction of any acyl group into atomic groupings containing active hydrogen resulting in the replacement of latter atoms in part or whole by the acyl group is known as acylation.

$$C_6H_5NH_2+(CH_3CO)_2 \rightarrow \underset{\text{acetanilide}}{C_6H_5NHCOCH_3}+CH_3COOH$$

Q. 8. Give the formula of phthalimide and say what type of compound it is.

Ans. 
$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$, it is a cyclic imide.

Q. 9. How many acyl groups are there in phthalimide?

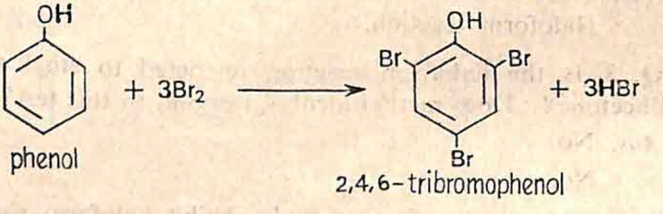
Ans. Two

Q. 10. Are the two terms 'acylation' and 'acetylation' synonymous?

Ans. No.

Q. 11. What happens, when phenol is treated with aqueous bromine?

Ans. Phenol forms 2, 4, 6-tribromophenol, which gets precipitated.



Q. 12. What is the product of halogenation of phenol by bromine, when CS_2 is used as a solvent?

Ans. Monohalogeno compound *p*-bromophenol is obtained.

$$\underset{\text{phenol}}{C_6H_5OH}+Br_2 \xrightarrow{\qquad\qquad} \underset{p\text{-bromophenol}}{BrC_6H_4OH\ (p)}+HBr$$

Q. 13. How can the phenol be separated from a carboxylic acid?

Ans. The mixture is treated with sodium hydroxide till it reacts alkaline. Carbon dioxide is then passed through the solution, when sodium phenoxide gets decomposed and phenol is liberated, but the salt of carboxylic acid remains unchanged in solution.

Q. 14. Which carries a specific sense and which a broad one:
acylation, acetylation?

Explain your answer.

Ans. Acylation conveys a broad sense, while acetylation a specific one.

For acylation see the ans. to Q. 7. When the group introduced is acetyl group ($CH_3CO—$), the general name 'acylation' is replaced by 'acetylation'.

Q. 15. (*a*) Pick out the reaction by which tri-iodomethane is prepared:

Acetylation, Acylation, Haloform reaction.

(*b*) Pick out the compound, which can be prepared by acetylation.

Phthalimide, Acetanilide, Iodoform

(*c*) Which is prepared from a cyclic anhydride:
phthalimide, iodoform?

Ans. (*a*) Haloform reaction, (*b*) Acetanilide, (*c*) phthalimide.

APPENDIX

1. *Atomic Weights of More Familiar Elements*

Atomic number	Name with Symbol	Atomic weight	Atomic number	Name with Symbol	Atomic weight
13	Aluminium *Al*	26·98	82	Lead *Pb*	207·21
51	Antimony *Sb*	121·8	3	Lithium *Li*	6·94
33	Arsenic *As*	74·9	12	Magnesium *Mg*	24·32
56	Barium *Ba*	137·37	25	Manganese *Mn*	54·93
83	Bismuth *Bi*	209·00	80	Mercury *Hg*	200·61
5	Boron *B*	10·82	42	Molybdenum *Mo*	96·00
35	Bromine *Br*	79·92	28	Nickel *Ni*	58·69
48	Cadmium *Cd*	112·41	7	Nitrogen *N*	14·01
20	Calcium *Ca*	40·08	8	Oxygen *O*	16·00
6	Carbon *C*	12·01	15	Phosphorus *P*	31·02
17	Chlorine *Cl*	35·46	78	Platinum *Pt*	195·23
24	Chromium *Cr*	52·01	19	Potassium *K*	39·10
27	Cobalt *Co*	58·94	14	Silicon *Si*	28·06
29	Copper *Cu*	63·60	47	Silver *Ag*	107·88
9	Fluorine *F*	19·00	11	Sodium *Na*	23·00
79	Gold *Au*	197·20	38	Strontium *Sr*	87·63
1	Hydrogen *H*	1·008	16	Sulphur *S*	32·07
53	Iodine *I*	126·92	50	Tin *Sn*	118·70
26	Iron *Fe*	55·84	30	Zinc *Zn*	65·38

2. REAGENTS

A. Some Common Acids

Concentrated Acids			Dilute Acids	
Name	Sp. gravity	Approximate normality	Preparation of dil. acid from conc. one	Approximate normality
Acetic acid, glacial	1·05	17*N*	Dilute with water 285 ml. of conc. acid to 1 litre.	5*N*
Hydrochloric acid	1·19	12*N*	Dilute with water 430 ml. of conc. acid to 1 litre.	5*N*
Nitric acid	1·42	16*N*	Dilute about 310 ml. of conc. acid with water to 1 litre.	5*N*
Sulphuric acid	1·84	36*N*	Add about 140 ml. of conc. acid slowly and very cautiously to about 500 ml. of water with constant stirring, cool and make up the volume to 1 litre with water.	5*N*

B. Some Common Bases

Name of the reagent		Approximate normality
ammonium hydroxide solution, concentrated		15*N*
Name of the reagent	Method of making the solution	
Dilute ammonium hydroxide solution	Dilute with water 335 ml. of the conc. solution to one litre.	5*N*
Sodium hydroxide solution	Dissolve by shaking 220 gms. of pellets or ordinary pure sticks of NaOH in water and make up the volume to one litre with water.	5*N*
Potassium hydroxide solution	Dissolve by shaking 310 gms. of pellets or ordinary pure sticks of KOH in water and make up the volume to one litre with water.	5*N*
Barium hydroxide	Mix about 70 gms. of crystallised barium hydroxide $Ba(OH)_2$ $8H_2O$ with one litre water, shake well, filter and protect, as far as practicable, from atmospheric CO_2.	0·4*N*
Calcium hydroxide solution	Mix about 3 gms. of calcium hydroxide with one litre water, shake well, filter and protect, as far as practicable from atomspheric CO_2.	0·04*N*

C. Some Salt Solutions

Name	Formula	Molecular weight	Grams in one litre	Normality (approx.)
Ammonium acetate	CH_3COONH_4	77	231	3N
Ammonium chloride	NH_4Cl	53·5	270	5N
Ammonium oxalate	$(NH_4)_2C_2O_4,H_2O$	142	35	0·5N
Ammonium sulphate	$(NH_4)_2SO_4$	132	132	2N
Barium chloride	$BaCl_22H_2O$	244	61	0·5N
Cadmium chloride	$CdCl_2,2H_2O$	219·4	55	0·5N
Calcium chloride	$CaCl_2,6H_2O$	219	55	0·5N
Cobalt nitrate	$Co(NO_3)_2.6H_2O$	291	44	0·3N
Ferric chloride*	$FeCl_36H_2O$	270	135	0·5N
Lead acetate	$Pb(CH_3COO)_2,3H_2O$	379	95	0·5N
Lead nitrate	$Pb(NO_3)_2$	331	165	1N
Mercuric chloride	$HgCl_2$	272	27	0·2N
Potassium chromate	K_2CrO_4	194	49	0·5N
Potassium dichromate	$K_2Cr_2O_7$	294	4·9	0·1N
Potassium ferricyanide	$K_3Fe(CN)_6$	329	55	0·5N
Potassium ferrocyanide	$K_4Fe(CN)_6.3H_2O$	422	53	0·5N
Potassium permanganate	$KMnO_4$	158	3·2	0·1N
Silver nitrate	$AgNO_3$	170	17	0·1N
Sodium acetate	$Na(CH_3COO),3H_2O$	136	408	3N
Di-sodium hydrogen-phosphate	$Na_2HPO_4,12H_2O$	358	120	1N
Ammonium Carbonate: Dissolve 160 gms. of the salt in one litre water containing 140 ml. of conc. ammonium hydroxide solution.				4N

D. Other Reagents

1. Ammonium molybdate $(NH_4)_6Mo_7O_{24},4H_2O$

Dissolve 50 gms. of the salt in a mixture of 70 ml. of conc. ammonia solution and 140 ml. water. When the substance has fully dissolved, add this solution very slowly and with vigorous stirring to a mixture of nitric acid and water (250 ml. conc. HNO_3+500 ml. water). Now dilute the solution to one litre and after allowing it to stand for 1-2 days decant the supernatant liquid from the top.

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*Dissolve 135 gms. of the salt in one litre water containing 20 ml. of conc. HCl.

2. Barfoed's reagent

Make 1% acetic acid solution and in 200 c.c. of this solution dissolve 13·3 gms. of pure copper acetate.

3. Bromine water

Prepare a solution by shaking 11 ml. of liquid bromine with one litre water. Saturated solution contains about 32·7 gms. of bromine per litre.

4. Chlorine water

Pass chlorine generated by dropping conc. HCl upon $KMnO_4$ crystals into water till saturation. Saturated solution contains 6·5 gms. of chlorine per litre.

5. Denige's reagent

Dissolve yellow HgO-powder in conc. H_2SO_4 (4 c.c. acid per gm. of HgO). Now pour this solution gradually and with stirring into water the volume of which is five times the volume of H_2SO_4 taken to dissolve the mercuric oxide.

6. Dimethyiglyoxime

Dissolve 1 gm. solid in 100 ml. absolute alcohol.

7. Diphenylamine

Dissolve 1 gm. solid in 100 ml. conc. H_2SO_4.

8. Fehling's solution

Solution A (blue). Dissove by shaking 34·6 gms. of pure $CuSO_4 . 5H_2O$ in water containing a few drops of conc. H_2SO_4 and make up the volume with water to 500 ml.

Solution B (colourless). Dissolve 175 gms. of Rochelle salt (*i.e.*, sodium potassium tartrate) and 70 gms. of pure NaOH in water and now dilute to 500 ml. with water.

The two solutions A & B are also described as no. 1 and 2 respectively. Mix the two solutions in equal volume *immediately* before use.

9. Fusion mixture

Mix dry Na_2CO_3 and K_2CO_3 in equal proportion.

10. Iodine solution.

Make a solution of 20 gms. pure KI in 30 ml. water. Now dissolve 12.7 gms. of iodine in this KI solution and then dilute to 1 litre with water.

11. Magnesia mixture

Dissolve 55 gms. $MgCl_2$ $2H_2O$ and 135 gms. of NH_4Cl in water, add 350 ml. of conc. ammonia solution; make up the volume with water to one litre.

12. Mercurous nitrate solution

Dissolve 200 gms. of mercury in *just* sufficient (moderately strong) nitric acid and then dilute to one litre with water. Keep a little metallic mercury in the bottle containing the solution.

13. Methyl orange

Dissolve about 0.5 g. in one litre of water.

14. Phenolphthalein

Dissolve 1 g. of the substance in 100 ml. alcohol and then add equal volume of water.

15. Potassium cyanide

Dissolve 32.5 gms. of the salt in one litre water.

16. Reinhardt reagent

Prepare a mixture of 250 ml. of water and 133 ml. of conc. H_2SO_4 and cool. Dissolve 67 gms. of crystallised manganous sulphate $MnSO_4.4H_2O$ in 250 ml. water, add carefully to it the cold acid solution as prepared above. Now add 133 ml. of syrupy phosphoric acid and then dilute to one litre with water.

17. Schiff's reagent

Make a dilute solution of rosaniline hydrochloride; add freshly prepared sulphurous acid solution with shaking till the colour is destroyed.

18. Sodium nitroprusside

Dissolve a crystal of about the size of a pea or even less in about 5 ml. water.

19. Stannous chloride

Dissolve 56 gms. of $SnCl_2.2H_2O$ in 100 ml. conc. HCl, dilute to one litre and keep a few pieces of metallic tin in the bottle containing solution.

20. Starch solution

Make a thin paste of 1-2 gms. of soluble starch with a little cold water and add 100 ml. of boiling water. Boil for about five to six minutes to get a clear solution. Add 2 gms. potassium iodide and 2-3 drops chloroform.

21. Sulphurous acid

Prepare a saturated solution of SO_2 in water.

22. Yellow ammonium sulphide $(NH_4)_2Sx$

Saturate 200 ml. of conc. ammonia solution with hydrogen sulphide in the cold. Add 10 gms. of flowers of sulphur and 200 ml. more of conc. ammonia solution, shake to dissolve all the sulphur and finally dilute to one litre.

E. Some Common Solid Chemicals

Aluminium turnings
Ammonium chloride
Ammonium nitrate
Borax
Calcium chloride (fused)
Calcium oxide
Cadmium carbonate
Copper turnings
Ferrous sulphate crystals
Iron nails
Iron powder
Lead carbonate
Microcosmic salt
Potassium hydrogen sulphate
Potassium carbonate
Potassium chlorate
Potassium dichromate
Potassium iodide
Potassium nitrate
Red lead
Silver nitrate
Silver sulphate
Sodium acetate
Sodium bicarbonate
Sodium bismuthate
Sodium carbonate
Sodium nitrate
Sodium nitrite
Sodium nitroprusside
Sodium peroxide
Sulphur, flowers
Starch
Tartaric acid
Tin foil
Urea
Zinc (granulated & pure)

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

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52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 2	3 4 5	6 7 7
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54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
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65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	2 3 4	4 5 6
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72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
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77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
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82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
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92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
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97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4

ANTILOGARITHMS

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·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0 0 1	1 1 1	2 2 2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0 0 1	1 1 1	2 2 2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0 0 1	1 1 1	2 2 2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0 1 1	1 1 2	2 2 2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0 1 1	1 1 2	2 2 2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0 1 1	1 1 2	2 2 2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0 1 1	1 1 2	2 2 2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0 1 1	1 1 2	2 2 3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0 1 1	1 1 2	2 2 3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0 1 1	1 1 2	2 2 3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0 1 1	1 2 2	2 2 3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0 1 1	1 2 2	2 2 3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0 1 1	1 2 2	2 3 3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0 1 1	1 2 2	2 3 3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0 1 1	1 2 2	2 3 3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0 1 1	1 2 2	2 3 3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0 1 1	1 2 2	2 3 3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0 1 1	1 2 2	2 3 3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0 1 1	1 2 2	3 3 3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0 1 1	1 2 2	3 3 3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0 1 1	2 2 2	3 3 3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0 1 1	2 2 2	3 3 3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0 1 1	2 2 2	3 3 4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0 1 1	2 2 2	3 3 4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0 1 1	2 2 2	3 3 4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0 1 1	2 2 3	3 3 4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0 1 1	2 2 3	3 3 4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0 1 1	2 2 3	3 4 4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0 1 1	2 2 3	3 4 4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0 1 1	2 2 3	3 4 4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0 1 1	2 2 3	3 4 4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0 1 1	2 2 3	3 4 4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0 1 1	2 2 3	3 4 4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1 1 2	2 3 3	4 4 5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 3	4 4 5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 3	4 4 5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1 1 2	2 3 3	4 5 5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1 1 2	2 3 4	4 5 5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1 1 2	2 3 4	4 5 5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1 1 2	2 3 4	4 5 6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1 1 2	3 3 4	4 5 6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1 1 2	3 3 4	4 5 6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1 1 2	3 3 4	5 5 6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1 1 2	3 3 4	5 5 6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1 1 2	3 3 4	5 5 6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1 1 2	3 4 4	5 6 6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1 1 2	3 4 4	5 6 6

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

TABLE OF

	Oxide or Hydroxide	Carbonate	Sulphide	Fluoride	Chloride
Silver	d.n.	d.n.	d.n.	w.	i
Mercurous	d.n.	d.n.	—	d.n.	c.n.
Lead	d.n.	d.n.	d.n.	d.n.	w.
Mercuric	d.h.	d.h.	a.r.	d.n.	w.
Bismuth	c.h.	d.h.	d.n.	d.h.	d.h.
Cuprous	c.h.	—	c.n.	c.h.	c.h.
Cupric	d.h.	d.h.	d.n.	d.h.	w.
Cadmium	d.h.	d.h.	d.h.	w.	w.
Stannous	d.h.	—	c.h.	w.	w.
Stannic	i.	—	c.h.	w.	w.
Arsenious	d.h.	—	c.n.	—	w.
Antimonious ...	d.h.	—	c.h.	w.	d.h.
Antimonic	c.h.	—	c.h.	w.	w.
Aluminium ...	d.h.	—	—	w.	w.
Chromic	d.h.	—	—	d.h.	w.
Ferrous	d.h.	d.h.	d.h.	w.	w.
Ferric	d.h.	—	—	w.	w.
Zinc	d.h.	d.h.	d.h.	w.	w.
Manganese ...	c.h.	d.h.	d.h.	d.h.	w.
Cobalt	c.h.	d.h.	c.n.	w.	w.
Nickel	d.h.	d.h.	c.n.	d.h.	w.
Calcium	w. : d.h.	d.h.	d.h.	i.	w.
Strontium	w. : d.h.	d.h.	d.h.	d.h.	w.
Barium	w.	d.h.	d.h.	d.h.	w.
Magnesium ...	d.h.	d.h.	d.h.	d.h.	w.

N.B. 1. All sodium, potassium and ammo
2. All nitrates and nitrites except bas
3. Natural silicates are generally inso
silicates, which have not been igni
4. Below is given the meaning of the

w.—water.
d.h.—dilute hydrochloric acid.
c.h.—concentrated hydrochlor
d.n.—dilute nitric acid.

SOLUBILITIES

Bromide	Iodide	Borate	Phosphate	Arsenite	Arsenate	Chromate	Sulphate
i	i	d.n.	d.n.	d.n.	d.n.	d.n.	w.
c.n.	c.n.	d.n.	d.n.	d.n.	d.n.	d.n.	d.n.
w	w.	d.n.	d.n.	d.n.	d.n.	d.n.	i.
w	c.n.	d.h.	d.h.	d.h.	d.h.	d.h.	d.h.
d.h.	d.h.	d.h.	d.h.	—	d.h.	d.h.	w.
c.h.	c.h.	—	—	—	—	—	—
w	—	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w	w.	d.h.	d.h.	—	d.h.	d.h.	w.
w	w.	d.h.	d.h.	d.h.	d.h.	—	w.
w	d.h.	—	c.h.	—	c.h.	—	—
—	—	—	—	—	—	—	—
d.h.	d.h.	—	—	—	—	—	—
—	—	—	—	—	—	—	—
w	w.	d.h.	d.h.	—	d.h.	d.h.	w.
w	—	d.h.	d.h.	w.	d.h.	—	w.
w	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w	—	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w	w.	d.h.	d.h.	d.h.	d.h.	d.h.	w.
w	w.	d.h.	d.h.	d.h.	d.h.	w.	w. : c.h.
w	w.	d.h.	d.h.	d.h.	d.h.	w.	i.
w	w.	d.h.	d.h.	d.h.	d.h.	d.h.	i.
w	w.	d.h.	d.h.	d.h.	d.h.	w.	w.

n salts are soluble in water.

trates and silver nitrite are soluble in water.

e; some, which are hydrated are decomposed by conc. HCl. But artificial undergo decomposition on treatment with dil. HCl.

reviations used in the above table:

c.n.—concentrated nitric acid
a.r.—aqua regia.
i.—insoluble.

id.

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